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FISSION OF ATOMIC NUCLEI—I

TRANSURANIUM ELEMENTS

This review of the transuranium elements is the first in a series of comprehensive and detailed articles by the author presenting internationally available data on nuclear fission.

A complete discussion of the subject will be accomplished by subsequent papers reviewing the field under the following general categories: Neutron Emission; Energetics of the Fission Process; Experimental Investigation of Energy Released in Fission; Cross Section of Fission; Unsymmetric, Symmetric and Triple Fissions; Identification of Fission Fragments; Fission Yield; Neutron Induced Fission of Other Heavy Elements; Fission of Nuclei by Particles Other Than Neutrons; Spontaneous Fission; and Utilization of Fission Energy.

These reviews describe the experimental and theoretical methods for obtaining the data presented.

By B. C. PURKAYASTHA

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IT IS WELL KNOWN that the total number of elements available from natural sources ranges from hydrogen to uranium, the atomic number of the latter being 92. In the past, many unsuccessful attempts were made to discover elements, from natural sources, having an atomic number higher than 92 (transuranic elements). With the discovery of the phenomenon of artificial radioactivity, and with the use of neutron beams for nuclear bombardment by Fermi and his co-workers in 1934 (*1*), new means were available for attacking the problem.

The two ultimate elements, uranium and thorium, when bombarded by neutrons, were found to develop β activity of a very complex nature. In fact, the decay curve for uranium showed four, and probably more, half-lives, indicating that four distinct β-ray bodies were formed. This observation suggested that the induced activity was due either to the new isotopic constituents of U or Th or, if only a single isotope was present, transuranic elements, which were undergoing successive β disintegrations, were being formed. It was also possible that the phenomenon was due to alternating α and β branch disintegrations. In the case of uranium, chemical analysis showed that none of the isotopes of elements 86–92 were formed; hence some transuranic elements ($Z >$ 92) were thought to have been formed. But the chemical properties of these hypothetical elements could only be theoretically predicted in an indefinite manner. According to prevailing ideas, they were thought to have properties similar to those of transitional elements rhenium-75, osmium-76, iridium-77 and platinum-78. However, there was an alternative hypothesis which stated that they might be analogous to the rare earths of the previous period

($_{57}$La–$_{71}$Lu) because of the formation of 5*f* shells by outer electrons.

Fermi (*2*) and his co-workers (1934) found that most of the activities could be precipitated with manganese dioxide and rhenium sulfide and concluded that transuranates represent a series similar to Re, Os, Ir, etc., of the third period.

I. Noddack (*3*), however, criticized Fermi's principle of chemical separation on the ground that such a chemical procedure overlooked the property of coprecipitation and adsorption and in no way excluded the possibility of the presence of elements of lower atomic number, as far as chemical evidence was concerned. The experimental evidence which she put forth to demonstrate the adsorption of elements on MnO_2 or rhenium sulfide were soon overthrown by the finer experimental technique of Hahn, Meitner and Strassmann (*4*, *5*) who proved beyond doubt that elements between 84 and 92 are not coprecipitated or adsorbed in their procedure. The possibility of the presence of elements of still lower atomic number was ruled out because no nuclear reaction was known which yielded more than two α's.

The general procedure adopted by the investigators for the separation of transuranates was to precipitate them all as sulfides in 2*N* HCl, using platinum as a carrier, and then to start their individual separation. As a result three different chains of transuranic elements were supposed to have been formed according to the scheme:

(1) $U^{238}(n,\gamma)U^{239} \xrightarrow[10\text{ s}]{\beta^-}$ $_{93}$eka-Re

$\xrightarrow[2.2\text{ m}]{\beta^-}$ $_{94}$eka-Os $\xrightarrow[59\text{ m}]{\beta^-}$ $_{95}$eka-Ir

$\xrightarrow[66\text{ h}]{\beta^-}$ $_{96}$eka-Pt $\xrightarrow[2.5^{\prime}\text{h}]{\beta^-}$ $_{97}$eka-Au (?)

(2) $_{92}U + n \rightarrow {}_{92}U \xrightarrow[40\text{ s}]{\beta^-}$ $_{93}$eka-Re

$\xrightarrow[16\text{ m}]{\beta^-}$ $_{94}$eka-Os $\xrightarrow[5.7\text{ h}]{\beta^-}$ $_{95}$eka-Ir (?)

(3) $_{92}U + n \rightarrow {}_{92}U \xrightarrow[23\text{ m}]{\beta^-}$ $_{93}$eka-Re (?)

The formation of so many transuranic elements was assumed to be due to successive emission of β^- rays by U^{239} and other isotopes of uranium. Curie and Savitch (*6*) investigated the β emission of the neutron-irradiated U and discovered the existence of a 3.5-h product. This could not be precipitated with Pt as a carrier as in the technique of Hahn, *et al*, (*4*, *5*) but could be precipitated with $_{57}$La.

The investigators thought that it was an isotope of $_{89}$Ac whose properties resemble those of $_{57}$La, but they were careful to mention that it might well be $_{57}$La. However, the experiments they performed were not decisive in proving whether the 3.5 -h product was La or Ac.

The observations of Curie and Savitch (*6*) were confirmed by Hahn and Strassmann (*7*), but they observed that, by using Ba as a carrier, they could isolate active bodies having half-lives of 25 m, 110 m and several days. From these came new daughter substances, having half-lives of 40 m, 4 h (3.5 h) and 60 h, which could be precipitated with La.

At first they thought that the products were $_{88}Ra^{231}$ and $_{89}Ac^{231}$, but there is the question of whether Ra can be produced in the process. It has to be supposed that U^{238}, after capture of the neutron, becomes $_{92}U^{239}$, which emits two α particles successively and becomes $_{88}Ra^{231}$, *i.e.*, we have a $(n,2\alpha)$ process. There was the further difficulty that three isotopes of Ra were found with half-lives of 14 m, 86 m and 300 h and possibly another with a half-life of 1 m. The investigators then thought that the active products labelled as Ra isotopes might as well have been Ba isotopes because Ra and Ba are so similar in their chemical properties. In order to test this point, the supposed Ra IV (half-life of 300 h)

was added to a solution containing Ba and a small quantity of isotopes of Ra, $MsTh_1$ or ThX was added. They then performed the fractional precipitation and crystallization used for separating Ra from Ba and found that the so-called Ra IV separated with Ba rather than with the $MsTh_1$ or ThX fraction.

The inevitable conclusion drawn by Hahn and Strassmann (*8*) was that the products which they had been calling radium isotopes were really Ba isotopes and their products were isotopic with La. The 86-m Ba has since been identified with a radioactive barium formed in the reaction $La^{139}(n,p)Ba^{139}$, and having a mass of 139. Similarly La, which comes from the barium isotope of 300-h half-life (Ra IV) probably has a mass of 140.

The investigators therefore concluded that, when U as well as Th is bombarded by neutrons, the nucleus divides into two fragments (fission). The reaction may be represented as:

$$_{92}U + {}_0n^1 \rightarrow {}_xA^{M_1} + {}_yB^{M_2} + a_0N^1$$

The fission fragments are denoted by *A* and *B*. The third term represents the subsequent discovery that a few neutrons are given out in the fission process. We should have

$$x + y = 92, M_1 + M_2 + a = 236 \text{ or } 239$$

The chemical procedure used was to precipitate the active product with a suitable carrier whose chemical properties were the same or similar to those of the active substance in question. But if the presence of two chemically similar elements, say Ba and Ra, were suspected, fractional crystallization with suitable indicators and the study of distribution of activities in different fractions were taken recourse to. Hahn also used a cyclic course of reactions to distinguish between barium and radium. Two elements may have similar chemical properties in some of their compounds, whereas in others, a marked change in solubility, adsorption and stability is generally observed. A fraction of barium chloride crystallized from a bombarded uranium solution was subjected to the following cyclic process:

(1) barium chloride → (2) barium succinate → (3) barium nitrate → (4) barium carbonate → (5) barium chloride → (6) barium ferrimannite → (7) barium chloride

The activity of the equal amounts of the product from the cyclic, as well as the control, preparations were compared and found identical.

Other experimental techniques were soon developed to identify the products chemically and establish genetic relations among them. Some authors [Bretscher (*9*), Meitner (*10*)] collected the fission fragments on a surface (filter paper, glass or water) placed at a small distance from a uranium layer irradiated with neutrons, and chemical examinations were performed on these collected samples. This form of collection is popularly known as the "recoil method." The other method of collection (bubbling method) introduced by Hahn and Strassmann (*11*) is based upon the fact that any noble gases formed (either as primaries or by subsequent β decay) can be continuously removed by bubbling air through a uranium solution during irradiation. The air is then passed through a wash bottle or absorption coal and the products collected can be subjected to various chemical separations. This simple device is in fact a powerful method of analysis. The elements identified in the collection under the experimental condition must have their origin in any one of the rare gases (Kr, Xe).

Convincing physical evidences in support of fission of the nucleus were soon put forward by a great number of investigators. In 1939 a group of workers [Frisch (*12*), Green (*13*),

Fowler (*14*), Roberts (*15*)] discovered heavily ionizing fission fragments amongst the products by the use of an ionization chamber connected to a linear amplifier. Tracks of these ionizing fission fragments were made visible by means of a cloud chamber [Corson, *et al.* (*16*), Joliot (*17*)] and also in the emulsion of photographic plates which were covered with uranium and exposed to neutrons [Myssowsky (*18*)]. These fission bits have been shown to emerge from the uranium nucleus and penetrate additional layers of materials [Joliot (*19*), McMillan (*20*), Meitner (*10*)]. It was soon discovered that the energy distribution of the fission fragments was not uniform but consisted of two well-defined energy groups [Jentschke (*21*), Booth (*22*)]. It was interpreted that the ratio of the two energy groups corresponds to the inverse ratio of the mass of the two fragments. Emission of neutrons has been found to accompany every fission process [Halban (*23*), Szilard (*24*), Anderson (*25*), Michiels (*26*), Droste (*27*)]. As a result of these technical developments, isotopes of elements from $_{35}$Br to $_{42}$Ma in the light group and from $_{51}$Sb to $_{57}$La in the heavy group were discovered within a year from the announcement of nuclear fission in January, 1939.

After the discovery of fission, the existence of Fermi's transuranates was open to serious doubt, since all the transuranic periods were found in the collection studied by the recoil method and many of these were chemically identified to be elements of lower atomic number. Further investigations showed that the periods assigned to transuranates by Fermi belong to fission fragments and as a consequence do not indicate the presence of any element beyond uranium.

The element uranium as it occurs in nature is a mixture of two isotopes U^{235} (0.72%) and U^{238} (99.28%) together with small amounts of U^{234} (or U II) formed from the successive disintegration of U^{238}. It was convincingly argued from a theoretical standpoint by Bohr (*28*, *29*) that fission with slow neutrons can almost be wholly ascribed to the rarer isotope U^{235}. This conclusion was confirmed by experiments with separated isotopes performed by Nier, Booth, and Dunning (*30*) and by Kingdon, Pollock, Booth and Dunning (*31*). Samples containing a few micrograms of uranium were separated into heavy and light fragments by means of a mass spectrograph. On subjecting these samples to slow neutron bombardment, the investigators observed fission in the light but not in the heavy isotope. It was found that the rare isotope U^{234} (U II) does not contribute appreciably to the fission effects. With separated isotopes [Booth, *et al* (*32*)] it has been confirmed that by bombardment with thermal neutrons a β^--active uranium isotope U^{239} is formed from U^{238}. The probability of formation of U^{236} from U^{235} was shown to be rather small.

Neptunium

The first transuranic element was discovered by McMillan and Abelson (*33*) at the University of California in 1940. Using neutrons from the Berkeley cyclotron they showed, by tracer technique investigations, that a radioactivity of 2.3-d half-life, formed during the irradiation of uranium with neutrons, is from the isotope 93^{239} which is the decay product of the 23-m 92^{239} formed by the capture of a neutron in U^{238}.

The chemical properties studied by the authors revealed that the element bore no resemblance to rhenium (element 75) for it is not precipitated by hydrogen sulfide in acid solution, is not reduced to metal by zinc, and does not have an oxide volatile at red heat. On the contrary, the authors showed that the new element is precipitated quanti-

tatively by hydrofluoric acid in presence of a reducing agent (sulfur dioxide), cerium being used as a carrier. In the presence of an oxidizing agent (bromate in strong acid) it is not precipitated as fluoride. In the reduced state with a thorium carrier it is precipitated by iodate, and in the oxidized state with uranium as sodium uranyl acetate. It is also precipitated with thorium on the addition of hydrogen peroxide, and in basic solution if carbonate is excluded.

These properties indicate that its two valency states are similar to tetra- and hexavalent states of uranium, the chief difference being in the value of oxidation potential between the two valencies such that the lower state is more stable in the new element. Later McMillan named element 93 "neptunium" in recognition of its position beyond, and chemical similarity to, uranium. The name comes from the planet Neptune which lies immediately beyond the planet Uranus in the solar system.

In 1942 Strassmann and Hahn (*34*) repeated the same type of experiments and separated Np^{239} from fission products with sodium uranyl acetate in presence of a strong oxidizing agent. Starke (*35*) employed Szilard and Chalmer's recoil method for the separation of U^{239} together with her daughter Np^{239}. Solid uranyl benzoyl acetone was irradiated with slow neutrons. In the enrichment process the U ions were adsorbed in $BaCO_3$ aqueous suspension, acetone being used as a solvent. The activity-time curve indicated one element of half-period 23 m belonging to U^{239} and one of half-period 2.4 d belonging to the disintegration product. Evidently the latter element is similar to uranium in its chemical properties. Bedreag (*36*) studied the analytical properties of Np^{239} by the tracer technique method and corroborated the work of McMillan (*33*).

The mechanism of the formation is as follows:

$$U^{238}(n,\gamma)U^{239} \xrightarrow[23\text{ m}]{\beta^-} Np^{239} \xrightarrow[2.4\text{ d}]{\beta^-} Pu^{239} \xrightarrow[24{,}000\text{ y}]{\alpha} U^{235}$$

The discoverer could not detect any α activity due to element 94 formed by β disintegration of neptunium. The α activity of element 94 was detected by Seaborg, which will be discussed later.

Neptunium-237. Another isotope of neptunium, Np^{237}, was discovered early in 1942 by Wahl and Seaborg (*37*, *38*) at the University of California. This isotope is the decay product of the previously known 7-d β-emitting U^{237} which is formed as the result of a $(n,2n)$ reaction on U^{238}. Np^{237} is important because of its α activity of very long half-life (2.25×10^6 y) and is therefore suitable as material for the investigation of the chemical properties of neptunium using weighable amounts and ordinary concentrations.

The first weighable amounts of Np^{237} were produced by the bombardment of large amounts of uranium with the fast neutrons from the cyclotron. The reaction for the production of this isotope is such that the yield is comparatively less than that for Pu^{239} and therefore the total amounts which were available for study were even smaller than the tiny amounts of Pu^{239} (discussed later). Nevertheless, L. B. Magnusson and T. J. La Chapelle at the Metallurgical Laboratory in Chicago were able, during 1944, to isolate the element in the form of pure compounds and to study a number of its important chemical properties. The chemical investigations were carried out with microgram amounts of the substance by the development of a special type of chemical technique known as "ultramicrochemistry" which will be discussed in a later article.

The piles at Clinton and Hanford, with their large neutron flux, produce much larger amounts of this isotope, and by means of special chemical extraction procedure, it was possible to extract

and make available for chemical studies more than 100 mg. Using this material J. C. Hindman, Magnusson and La Chapelle were able to make an intensive study of the chemical properties of neptunium leading to the establishment of its oxidation states and the preparation of a number of its compounds. S. Fried, N. R. Davidson and A. E. Florin are responsible for a considerable amount of the investigation of the dry chemistry of this element.

Investigations have shown that neptunium has the oxidation states III, IV, V and VI with the lower oxidation states relatively more stable than those of uranium, but less so than those of the next higher element, plutonium.

The isotope Np^{237} is of particular interest because of its availability in weighable amounts. Thus it has been possible to measure its cross section for the absorption of thermal neutrons, *i.e.*, for the reaction $Np^{237}(n,\gamma)Np^{238}$. The value obtained by A. H. Jaffey and Magnusson is 200 barns. It has also been possible to test this isotope for thermal neutron fissionability and according to A. Ghiorso and Magnusson, this isotope does undergo fission with thermal neutrons with a cross section of about 0.02 barn. The discovery of Np^{237} has solved the question of existence of a $4n + 1$ radioactive chain, which will be discussed later.

Of the transuranic elements isolated in weighable amounts, the isotope Np^{237}, because of its relatively low specific alpha activity, forms a class by itself. The half-life of Np^{237}, 2.25×10^6 y, corresponds to a specific alpha-particle activity of some one and a half million alpha particles per minute per milligram, about one thousand times that of ordinary uranium. Material of this order of radioactivity can be handled without special equipment. It is hoped that when Np^{237} will be available in abundant quantities, it may be used sparingly in university laboratory courses in qualitative analysis and advanced inorganic chemistry and in courses on nuclear chemistry and physics [Seaborg (*40*)].

Neptunium-238. Another β^--active isotope Np^{238}, of half-life 2.0 days, was discovered by Seaborg, *et al*, (*41, 42*) at the University of California during late 1940 and early 1941 by bombarding uranium with deuterons in the Berkeley cyclotron. The other isotopes of neptunium, with mass numbers 234, 235, and 236, have been obtained by bombarding uranium with highly energetic deuterons and alpha particles in the recently rebuilt Berkeley 60-inch cyclotron. Table 1, based on Seaborg's paper on the transuranic elements (*37*), illustrates the interesting nuclear reactions that take place in the formation of these isotopes.

Plutonium

After neptunium, the next transuranium element to be discovered was that of atomic number 94. It has already been mentioned in connection with Np^{238} that Seaborg, *et al*, (*41, 42*) bombarded U^{238} with deuterons and discovered that the isotope Np^{238} was formed by the $(d,2n)$ reaction. This isotope of element 93 decays by β^- emission into an alpha-emitting isotope of element 94 (Pu^{238}). This alpha emitter has a half-life of about 50 years. The early experiments performed by tracer technique indicated that the activity is chemically separable from uranium and neptunium.

The 50-year activity can be precipitated in what is called the +4 valence state as fluoride, or iodate or as a peroxy-hydrate by using thorium as a carrier material. In the presence of the extremely strong oxidizing agent, persulfate ion (S_2O_8), plus Ag as a catalyst, this radioactive isotope is oxidized to a higher valence state which does not precipitate as fluoride. The oxidizing bromate ion is not sufficiently

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TABLE 1

Nuclear Reactions and Isotope Properties

Isotope		Activity observed or possible	Half-life	Target nuclei for transmutation																	α-decay descendant of	β-decay descendant of	Ref.	Remarks
Z	A			n,γ	n,2n	n,p	n,α	d,p	d,α	d,n	d,2n	d,3n	d,4n	α,n	α,2n	α,3n	α,p	α,pn	α,p2n	α,p3n	α,p4n				
90	RdAc[227]	α,γ	18.9 d																			Ac[227]		
	RdTh[228]	α,γ	1.9 y																			MsTh[228]		
	Th[229]	α	7×10^3 y																		U[233]			e
	Io[230]	α,γ	8.3×10^4 y																		U II[234]			
	UY[231]	β⁻	24.6 h		Th[229]																U[235]		49	
	Th[232]	α	1.39×10^{10} y																					a,f
	Th[233]	β⁻	23 m	Th[232]																			49	
	UX_1[234]	β⁻,γ	24.5 d																		U I[238]			
	*Th[235]	β⁻					U[235]																	
91	*Pa[229]	K										Th[230]								Th[230]				
	*Pa[230]	K,α			Pa[231]						Th[230]													
	Pa[231]	α,γ	3.2×10^4 y																			UY[231]		
	*Pa[232]	β⁻		Pa[231]				Pa[231]	U[234]		Th[232]									Th[232]				
	Pa[233]	β⁻,γ,ε⁻	27.4 d																		Np[237]	Th[233]		e
	UZ[234]	β⁻,γ	6.7 h																					g
	UX_2[234]	β⁻,γ,I.T.	1.14 m																			UX_1[234]		
	*Pa[236]	β⁻				U[235]																		
	*Pa[238]	β⁻							U[238]															
92	*U[231]	K									Pa[231]					Th[230]				Pa[231]				
	*U[232]	α								Pa[231]					Th[230]				Pa[231]					
	U[233]	α	1.6×10^5 y																			Pa[232]	72	e,h
	U II[234]	α	2.69×10^5 y																		Pu[238]	Pa[234]		b
	AcU[235]	α	7.07×10^8 y																		Pu[239]			c,f
	*U[236]	α					Pu[239]	U[235]																
	U[237]	β⁻,γ	6.8 d		U[236]																		49	
	U I[238]	α	4.51×10^9 y																					d,f
	U[239]	β⁻	23 m	U[238]																			49	
93	*Np[232]	β⁺										U[233]								U[233]				
	*Np[233]	K									U[233]									U[233]				
	Np[234]	K	4.4 d									U[235]		Pa[231]						U[235]			77	

	Np^{235}	K	240 d								U^{235}				U^{235}														57		
	Np^{236}	β^-	20 h							U^{235}				U^{235}								U^{235}							57		
	Np^{237}	α	2.25×10^6 y																						Am^{241}	U^{237}		57		e,h
	Np^{238}	β^-	2.0 d								U^{238}								U^{235}				U^{238}						57		
	Np^{239}	β^-	2.3 d							U^{239}												U^{238}					U^{239}		57		
	*Np^{240}	β^-																		U^{236}											
	*Np^{241}	β^-																	U^{238}												
94	*Pu^{234}	α, K															U^{233}														
	*Pu^{235}	β^+												Np^{237}		U^{233}															
	*Pu^{236}	α										Np^{237}			U^{233}	U^{234}	U^{235}							Np^{237}	Cm^{243}	Np^{238}				
	*Pu^{237}	K									Np^{237}				U^{234}	U^{235}						Np^{237}								
	Pu^{238}	α	50 y																					Cm^{242}	Np^{238}	57				
	Pu^{239}	α	24,000 y																						Np^{239}	57		h		
	*Pu^{240}	α							Pu^{239}							U^{235}		Np^{237}													
	Pu^{241}	β^-	long												U^{236}													40		e
95	*Am^{237}	β^+												Pu^{239}																	
	*Am^{238}	β^+											Pu^{239}				Np^{237}						Pu^{239}								
	*Am^{239}	β^+ or K									Pu^{239}					Np^{237}						Pu^{239}								
	*Am^{240}	β^+ or β^-			Am^{241}					Pu^{239}				Np^{237}							Pu^{239}										
	Am^{241}	α	500 y																							Pu^{241}		40		e,h
	Am^{242}	β^-	18 h	Am^{241}																								40		
96	*Cm^{239}	β^+												Am^{241}																	
	Cm^{240}	α	30 d														Pu^{239}												37		
	*Cm^{241}	β^+														Pu^{239}						Am^{241}								
	Cm^{242}	α	150 d												Pu^{239}											Am^{242}		37, 49a	h	
	*Cm^{243}	α																Am^{241}													
	*Cm^{244}																Am^{241}														
97	*X^{242}	β^+ or K														Am^{241}															
	*X^{243}	β^+														Am^{241}															
	*X^{244}	β													Am^{241}																

* Nuclei as yet unknown.

[a] Percentage abundance = 100.

[b] Percentage abundance = 0.006.

[c] Percentage abundance = 0.71.

[d] Percentage abundance = 99.28.

[e] Member of $(4n + 1)$ series.

[f] Natural source.

[g] UX_2^{234} I. T.

[h] Has been isolated in weighable amounts.

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powerful to oxidize it to its higher valence state, hence the radioactivity comes down as a fluoride even in presence of bromate ion. With the help of the persulfate ion it has been possible to separate quantitatively this activity from thorium by using β-active UX_1 as an indicator for thorium.

These early experiments with tracer amounts of this material showed that element 94 also has at least two oxidation states, an upper state (or states) and a lower state (or states). The experiments further indicated that even stronger oxidizing agents are required to oxidize element 94 to the upper from the lower state, than is the case for neptunium. Element 94 was given the name plutonium in accordance with the convention which was used in the naming of neptunium.

Plutonium-239. The most important isotope of plutonium is, of course, the isotope of mass 239. This isotope, Pu^{239}, which is the daughter of 2.3-d Np^{239}, was discovered by Kennedy, Seaborg (*37*, *38*), Segré and Wahl in 1941. It is an alpha-emitter with a half-life of about 24,000 years. Its tremendous importance is due to its property of having a fission cross-section value near that of U^{235}. Once the potentiality of this isotope as atom-bomb material was definitely established, the paramount problem was that of producing it on a large scale. The attempts on large scale production resulted in the construction of self-sustaining piles or reactors, the details of which will be discussed later. The separation of plutonium from the huge amounts of uranium and other fission fragments produced in the piles required a thorough study of the chemistry of plutonium. Such a thorough study could not be made by reliance upon the data obtained by the following of a tracer technique course of investigation.

A pure compound of plutonium, free from carrier material and all other foreign matter, was prepared by B. B. Cunningham and L. B. Werner at the Metallurgical Laboratory in Chicago on August 18, 1942. This masterpiece of chemical work was accomplished with only a couple of micrograms of plutonium produced by the bombardment of uranium by neutrons from the Berkeley cyclotron. This is the first instance of the isolation of an artificially made radioactive isotope in weighable amounts.

During the summer of 1942 large amounts of uranium (hundreds of pounds) were bombarded for several months in the cyclotrons of the University of California, Berkeley, and Washington University, St. Louis. This resulted in the production of two hundred micrograms of plutonium and made it possible to extend considerably the program of ultramicrochemical investigations. In September, 1942, Cunningham and Werner were able to prepare a number of compounds of pure plutonium and to determine by means of chemical analysis that, in solution, plutonium is most stable in its tetravalent state. W. M. Latimer, A. C. Wahl, J. W. Hamaker, and G. E. Sheline also contributed to this ultramicrochemical program of investigation and were able to show that the highest oxidation state of plutonium is VI. In addition R. E. Conniek established the existence of a trivalent state. Until the end of 1943, these cyclotron bombardments were the only source of plutonium, and during this period of time about 1,000 μgm or 1 mg of plutonium was prepared. This material was used to maximum advantage by the ultramicrochemists to prepare compounds of plutonium and to measure properties such as solubilities and oxidation potentials.

In connection with the separation process it was necessary to determine a number of physical and chemical properties of the dry salts of plutonium

and of plutonium metal. The ultramicro scale of investigation was applied to this branch of study as well. A number of compounds were prepared by reactions involving solid and gas phases, that is, by dry chemical reactions. This work was done in collaboration with W. H. Zachariasen, of the University of Chicago staff, who was able to use his X-ray technique to identify, or help identify, a number of compounds which were synthesized. Thus in many cases, their chemical structure was established. It was also possible to prepare metallic plutonium and study some of its properties by taking recourse to ultramicrochemical scale of investigations.

As is now well known, large quantities of plutonium are available as the result of operation of the chain-reacting units at Clinton and Hanford. Using plutonium from these sources, a number of groups have thoroughly investigated the properties of plutonium. All phases of plutonium chemistry, with special reference to purification, separation, oxidation states, potentials, reaction kinetics and complex ion formations, have been intensely studied.

The work has established that plutonium has the oxidation states III, IV, V, VI and that the lower oxidation states tend to be more stable than is the case for neptunium. The chemistry of plutonium has been so thoroughly studied that Seaborg (*40*) has remarked, "It is fair to say that chemistry of plutonium today is as well understood as, or better understood than, that of most of the elements in the periodic system."

Pu^{239} has a high specific alpha radioactivity, amounting to about 140×10^6 disintegrations per minute per milligram. From such considerations special precautions and equipment are necessary for its investigation. This high alpha radioactivity makes it expedient to continue to use small amounts, that is, milligram amounts, for a number of investigations even though large amounts might be available.

Americium and Curium

Elements with atomic numbers 95 and 96 have been synthesized by Seaborg (*37, 40*), R. A. James, L. O. Morgan and A. Ghiorso. U^{238} and Pu^{239} were bombarded with high-energy (40–44 Mev) helium ions in the Berkeley 60-inch cyclotron. The mechanism of the reactions have been pictured as follows:

$$U^{238}(\alpha,n)Pu^{241} \xrightarrow[\text{long-lived}]{\beta^-} Am^{241} \xrightarrow[500\ y]{\alpha} \quad (1)$$

$$Pu^{239}(\alpha,3n)Cm^{240} \xrightarrow[30\ d]{\alpha} \quad (2a)$$

$$Pu^{239}(\alpha,n)Cm^{242} \xrightarrow[150\ d]{\alpha} \quad (2b)$$

Chemical properties studied by the tracer technique method indicate that the trivalent state is the most stable and by far the most important state for these elements in aqueous solution. In fact in the case of element 96 the evidence indicates that the III state is the only one that exists in aqueous solution. The investigators have considered the transuranic elements as members of an actinide series (discussed subsequently) analogous to the lanthanide series of the previous period. Thus, these two actinide elements are given names by analogy with the corresponding numbers of the "lanthanide" earths. They have suggested for element 95, with its $5f^6$ electrons, the name "americium" (symbol Am), after the two Americas or New World, this by analogy with europium, with its $4f^6$ electrons, which was named after Europe. For element 96, containing $5f^7$ electrons, they have suggested "curium" (symbol Cm), after Pierre and Marie Curie the pioneer investigators in the field of radioactivity; this is by analogy with gadolinium, which con-

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tains $4f^7$ electrons and recalls Gadolin, the great investigator of the rare earths.

Americium, with its 500-year half-life, has a higher specific alpha activity than plutonium. Its specific alpha activity amounts to some 70×10^9 alpha disintegrations per minute per milligram. The investigation of the chemical properties of americium will demand investigators who are well trained in handling highly alpha-active materials. The isotope Cm^{242} with its 150-day half-life has a specific alpha activity corresponding to about 10^{14} alpha disintegrations per minute per milligram. When the technical difficulty of producing such a relatively short period in microgram amounts is overcome, other difficulties will be the rapid decomposition of water in the solution, the formation of hydrogen peroxide in the solution, heating of the solution and other effects.* Seaborg (*40*), however, speculates that isotopes such as Cm^{243}, Cm^{244}, Cm^{245} or Cm^{246} may have longer half-lives and these isotopes may eventually become available for investigation.

B. B. Cunningham working at the Metallurgical Laboratory has succeeded in isolating Am^{241} and in studying its chemical properties using a weighable amount on the ultramicrochemical scale. The work of Cunningham and L. B. Werner with pure americium in aqueous solution has confirmed the tracer work by showing that the III oxidation state is very stable in solution and is the predominant and most important state.

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* *Note added in proof:* Cm^{242} (150 d) has recently been isolated in weighable amounts by placing Am^{241} in a high neutron flux pile. The ultramicro quantity of curium, formed by the reaction $Am^{241}(n, \gamma)Am^{242} \xrightarrow[18h]{\beta^-} Cm^{242}$, was separated from americium by the use of ion-exchanging resin. The study of absorption spectra and chemical properties in the ultramicro scale by Werner and Perlman (49a) has set forth conclusive evidence that curium is a typical trivalent element and a close analogue of gadolinium.

Ultramicrochemistry

Artificially radioactive substances are produced in unweighable amounts. The only way to investigate these submicroscopic, invisible and unweighable amounts was the tracer technique introduced by Hevesy in the course of his investigations with natural radioactive substances. The deductions concerning the chemical nature of an active substance are only possible when the compound of the carrier element and that of the element to be carried display true isomorphism. The fact that an activity is carried down with a carrier does not always mean a chemical homology or analogy between the active element and the carrier in question. An activity may be carried down by adsorption or because of anomalous mixed crystal formations. Thus evidences derived from tracer chemistry are of secondary nature and cannot be unflinchingly applied to a separation plant for actual isolation of plutonium. Another factor in the application of tracer chemistry in a separation plant for plutonium is the actual concentration of plutonium produced in the pile. No method of separation can be safely recommended unless, and until, it is practiced at the actual concentrations of plutonium which would exist in the large scale separation plant. It was anticipated at the time that a few micrograms of plutonium could be made available by neutron bombardment of uranium in the cyclotron and the novel idea of attempting to work with microgram amounts of plutonium, but at the same time with ordinary concentrations, was adopted.

By using extremely small volumes and by weighing microgram amounts of plutonium it was possible to reach relatively high concentrations even with microgram quantities of materials. In the ultramicrochemical scale of operation extremely small volumes of the

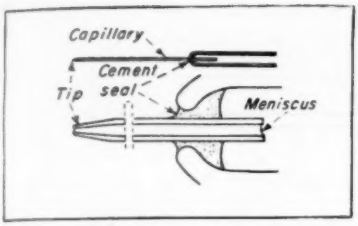

FIG. 1. Ultramicro volumetric pipette (*38*)

order of 10^{-1} to 10^{-5} cc can be handled with the help of specially constructed small capillary containers, pipettes, burettes and micromanipulators. Liquid volumes of the order of range stated above are measured within an accuracy of 1 % by means of fine calibrated capillary tubing, the movement of liquid within capillary being governed by air pressure under sensitive control. The smaller pipettes may be constructed to fill automatically by capillary attraction (Fig. 1). The test tubes and beakers for this purpose are made out of capillary tubing which has an inside diameter of 0.1 to 1 mm. The weights of solids which are handled in reagents and precipitates are usually in the range of 0.1 to 100 μgm. The work is usually done on the mechanical stage of a microscope, with the entire apparatus within the field of view (Fig. 2). The test tubes, pipettes, etc. are handled by means of mechanical aids known as micromanipulators. Precision of the order of 0.5 % is easily secured in work of this scale. The separation of solids from liquids is usually done by means of centrifugation rather than by filtration.

Specially designed highly sensitive balances are used in this scale of operation. One type of balance which is used in the weighing experiments is the Salvioni balance (Fig. 3). This balance consists of a very thin quartz fiber fastened to a solid base at one end to which is attached, at right angles at the other end, a small holder for the sample

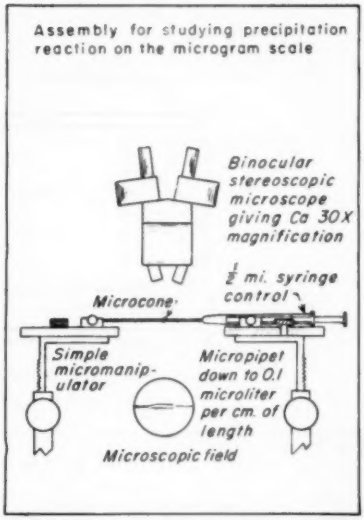
Assembly for studying precipitation reaction on the microgram scale
Binocular stereoscopic microscope giving Ca 30X magnification
½ mi. syringe control
Microcone
Simple micromanipulator
Micropipet down to 0.1 microliter per cm. of length
Microscopic field

FIG. 2. Study of precipitation reaction on ultramicro scale (*38*)

to be weighed. The measurement of the weight of the sample depends upon the measurement of the amount of bending of the quartz fiber arm, and the balance is usually calibrated by the use of known weights. The Salvioni balance has a sensitivity of 0.02 μgm, a weighing range of 20 μgm and a capacity of 10.5 mg.

Another type of balance used in ultramicro scale of operation has an extremely high sensitivity. This balance, designed by P. L. Kirk, can weigh amounts as small as 1 μgm or less with an accuracy of 0.02 μgm (Fig. 4). The material can be in containers weighing at least as much as 25 mg. The beam and other operating parts of this balance are constructed of fibers of pure quartz, ranging in diameter from about four times that of a human hair down to fibers which are invisible to the unaided eye. The beam of the balance is a quartz fiber framework about four inches in length which is suspended in-

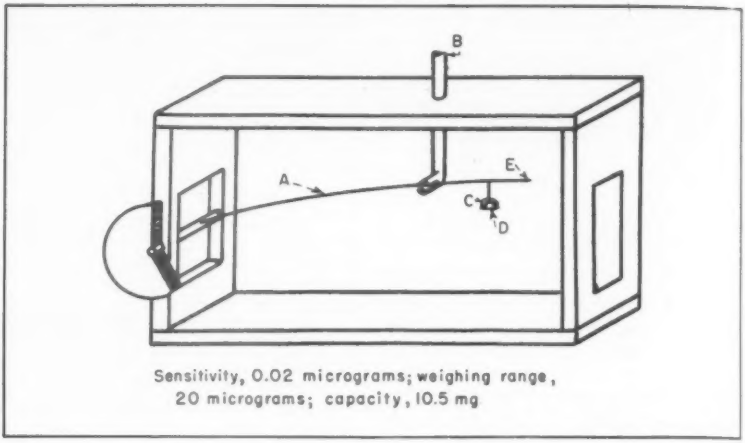

FIG. 3. The Salvioni balance (*38*)

side a brass housing on a horizontal fiber at right angles to the direction of the beam. From each end of the beam there hangs a fiber to which is attached a quartz frame holding a weighing pan of thin platinum foil. Substances to be weighed are placed on the foil. The addition of a weight to one side of the balance causes the beam to be depressed on that side. The beam is restored to its initial position by twisting in the opposite direction on the fiber which supports it. The torsion applied in order to return the beam to its initial position, after the addition of a weight, is measured and used to evaluate the weight added. The movements of the beam are magnified by a suitable optical arrangement and all parts of the balance are protected against the slightest air currents.

The method of separation recommended by the study of the ultramicro scale of investigation was first tried at the Hanford plant and the success surpassed expectations though the scale-up between the ultramicrochemical experiments to the Hanford plant amounts to a factor of about 10^{10}.

It is now known that a very small amount of a foreign substance exerts great influence upon hardness, ductility and durability of metals. In the life process of plants, as well as of animals, substances present in minute amounts often play a much greater role than do substances occurring in easily determinable quantities. In other fields of studies as well, the determination of traces is a serious problem. The estimation of traces or even their detection has solved many problems otherwise unassailable. Paneth's remarkable conclusion that meteorites probably originated within our solar system and not—as was previously assumed—from fixed stars outside that system depended on an accurate determination of as little as 2×10^{-11} gm of helium in iron meteorites. That there is a subterranean connection between the Danube and Rhine rivers was established by the use of fluorescein. Ultramicrochemical technique is a great advance in the study of those minute quantities which are termed unweighables, and its application in different fields of study augurs well for scientific progress.

Electronic Structure of the Actinide Series

It is well known that the chemical properties of elements have now been satisfactorily explained from the electronic structure of outer incompleted shells. Table 2, reproduced from "Treatise on Modern Physics" (*43*) with changes, shows the electronic structure of the actinide series.

The elements are grouped into: (1) regular series, (2) transitional series (3) and rare earth series. Their electron compositions are:

1. Regular group: $(ns)^x(np)^y$, $x = 1$ to to 2; $y = 1$ to 6.
   Groups exist for $n = 2, 3, 4, 5, 6$.
2. Transitional group: $(nd)^x[(n+1)s]^y$, $x = 1$ to 10; $y = 1$ to 2.
3. Rare earth group: $(4f)^x \begin{cases} 5d6s^2 \\ 5d^26s \end{cases}$; $x = 1$ to 14.

There are three transitional groups, which can be defined as the elements in which the *d*-shell is being filled up:

$_{21}$Sc to $_{29}$Cu,	$n = 3$
$_{39}$Y to $_{47}$Ag,	$n = 4$
$_{71}$Lu to $_{79}$Au,	$n = 5$

TABLE 2

Electron Composition of Typical Levels

$_{57}$La	$5d6s^2$	$_{89}$Ac	$6d7s^2$
$_{58}$Ce	$5d^26s^2$ $4f5d6s^2$	$_{90}$Th	$6d^27s^2$ $5f6d7s^2$
$_{59}$Pr	$4f^25d6s^2$	$_{91}$Pa	$6d^27s^2$ $5f6d^27s^2$ $5f^26d7s^2$
$_{60}$Nd	$4f^35d6s^2$	$_{92}$U	$6d^47s^2$ $5f^26d^27s^2$ $5f^36d7s^2$
61	$4f^45d6s^2$	$_{93}$Np	$5f^36d^27s^2$ $5f^46d7s^2$
$_{62}$Sm	$4f^55d6s^2$	$_{94}$Pu	$5f^46d^27s^2$ $5d^56d7s^2$
$_{63}$Eu	$4f^65d6s^2$	$_{95}$Am	$5f^66d^27s^2$ $5f^77s^2$
$_{64}$Gd	$4f^75d6s^2$	$_{96}$Cm	$5f^66d^27s^2$ $5f^77d7s^2$

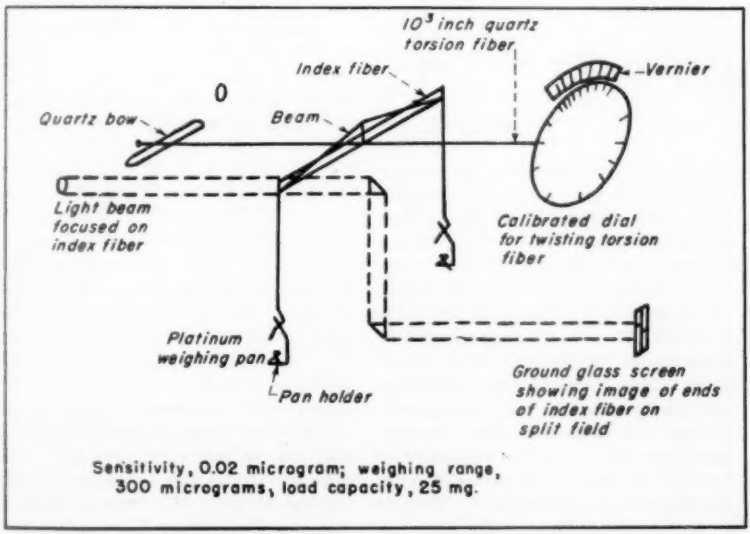
10³ inch quartz torsion fiber
Index fiber
Vernier
0
Quartz bow
Beam
Light beam focused on index fiber
Calibrated dial for twisting torsion fiber
Platinum weighing pan
Pan holder
Ground glass screen showing image of ends of index fiber on split field
Sensitivity, 0.02 microgram; weighing range, 300 micrograms, load capacity, 25 mg.

FIG. 4. Quartz fiber torsion balance (*38*)

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TABLE 3

Electron Composition of Typical Levels

$_{72}Hf$	$4d^{10}4f^{14}$ $5d^{2}6s^{2}$	$_{90}Th$	$4d^{10}4f^{14}$ $5d^{10}$ $6d^{2}7s^{2}$
$_{73}Ta$	$5d^{3}6s^{2}$	$_{91}Pa$	$6d^{3}7s^{2}$
$_{74}W$	$5d^{4}6s^{2}$	$_{92}U$	$6d^{4}7s^{2}$
$_{75}Re$	$5d^{5}6s^{2}$	$_{93}Np$	$6d^{5}7s^{2}$
$_{76}Os$	$5d^{6}6s^{2}$	$_{94}Pu$	$6d^{6}7s^{2}$
$_{77}Ir$	$5d^{7}6s^{2}$	$_{95}Am$	$6d^{7}7s^{2}$
$_{78}Pt$	$5d^{8}6s^{2}$	$_{96}Cm$	$6d^{8}7s^{2}$

The nd and $(n + 1)s$ levels appear to be equally probable and there are states corresponding to one electron or two electrons in the s-shell. The border elements, such as Cu, or Ag, show other properties not belonging to this group because of complete filling of d-shells.

Rare earths can be defined as those elements which are having their f-shells filled up. There is, so far, only one rare earth group, from $_{57}La$ to $_{71}Lu$; in La the constitution is $5d6s^2$, and in Ce, $5d^26s^2$, but $4f5d6s^2$ is also known spectroscopically. After that the composition is

$$(4f)^x \begin{cases} 5d6s^2 \\ 5d^26s \end{cases}; \qquad x = 1 \text{ to } 14.$$

It is a question of whether $_{89}Ac$ and the elements following it would have the rare earth structure or transitional group structure. The possibilities are presented in Table 2.

In consideration of the facts that $_{89}Ac$ was known to be similar to $_{57}La$, and $_{90}Th$ and $_{91}Pa$ have a certain amount of resemblance to $_{72}Hf$ and $_{73}Ta$, Fermi proposed that these elements and those which he thought he had prepared by neutron bombardment have transitional group structure. He gave to elements 93 to 96 the names eka-Re, eka-Os, eka-Ir, and eka-Pt. Fermi's proposals are presented in Table 3.

The first members ($_{90}Th$, $_{91}Pa$) of the group 90–96 show a certain amount of resemblance in chemical properties to the first members ($_{72}Hf$, $_{73}Ta$) in the $5d$ transition series, but the members of the former ($_{92}Np$, $_{94}Pu$, $_{95}Am$, $_{96}Cm$) have been found, as described, to have no resemblance to $_{75}Re$, $_{76}Os$, $_{77}Ir$, $_{78}Pt$ and to corresponding members of the $4d$ and $3d$ transitional series. Hence the proposed electron composition as shown in Table 3 has to be abandoned.

The second hypothesis on the electronic structure of the transuranium elements is that of A. V. Grosse (*44*). His idea was based on Bohr's (*45*) "second group" of the rare earths. The author, from a study of the electronic arrangement in uranium and its neighbors in the period, predicted the existence of a $5f$-shell building group with uranium as the first member, just as cerium is the first member of the rare earth group in the previous period. According to Grosse the transuranic elements, instead of having properties similar to higher homologues of Re and Os, etc., seem to be more on the border of uranium, the series being analogous to the rare earths but chemically dissimilar to them. According to Grosse the electronic structure of uranium and transuranic elements is as follows:

$_{92}U$	$5f^{3}6d^{1}7s^{2}$
$_{93}Np$	$5f^{4}6d^{1}7s^{2}$
$_{94}Pu$	$5f^{6}6d^{0}7s^{2}$

As has been observed in the case of lanthanides, the rare earths, from praseodymium upwards, show greater similarity in chemical properties to La than to Ce. In this group too, according to Grosse, Np and other transuranic elements should be more akin to Pa than to U. However, similarity of transuranic elements, especially of Np and Pu to uranium, has been well established and this is a serious point against Grosse's idea that uranium is the first element for $5f$ transition and contains one $5f$ electron.

To overcome this difficulty K. Starke (*46*) argued that thorium differs too widely to be the first member of a group of thorides analogous to the lanthanides and concluded that there is more evidence that uranium may be the first member of a group of uranides. Uranium would then have six electrons in 6*d* and 7*s* levels, and elements 93 and above would be formed by filling in the 5*f* group. From this point of view, the element $_{93}$Np has seven outer electrons of which six are as in uranium ($6d^47s^2$) while the seventh is incorporated as a 5*f* electron. The electronic structures are as below:

$_{92}$U	$6d^47s^2$
$_{93}$Np	$5f6d^47s^2$
$_{94}$Pu	$5f^26d^47s^2$

Starke's idea accounts for the similarity of Np and Pu to uranium and explains the hexavalency of these elements without affecting the 5*f* electrons. However, the hypothesis cannot explain why $_{96}$Cm should be only trivalent.

From a theoretical standpoint M. Goeppert-Mayer (*47*) has discussed, by calculation of the atomic proper functions of the 4*f* and 5*f* electrons, the possibility of the existence of a second rare earth group beginning with uranium and extending to the transuranic elements. The theory predicts the occurrence of a second rare earth group in the neighborhood of $Z = 92$.

Such an idea that the first 5*f* electron enters either at uranium or at neptunium (93) cannot explain the chemical properties of the whole series. The feature that a 6*d* transition at the beginning and a 5*f* transition before the 6*d* shell is fully saturated with ten electrons does not corroborate the arrangement of the previous period.

Seaborg (*37*, *38*) points out that the dissimilarity of $_{93}$Np and $_{94}$Pu to $_{75}$Re and $_{76}$Os suggests that it is the 5*f* electron shell which is being filled, although it is not possible to deduce from this chemical evidence alone whether uranium is the first element in the series for which this is the case. He puts forth the attractive hypothesis that the rare earth series begins with actinium just as the lanthanum series of the previous period. On this basis the first 5*f* electron appears in thorium. Thus the characteristic oxidation state, *i.e.*, the valency exhibited by those members with seven 5*f* and fourteen 5*f* electrons, for this transition series is 3. The tetravalency demonstrated by thorium is then analogous to the IV oxidation state of cerium. From the behavior of uranium, neptunium and plutonium it may be deduced that as many as three of the assumed 5*f* electrons are readily given up, so that the failure of thorium to demonstrate an oxidation state III is accounted for. On the basis of this hypothesis elements 95 and 96 should exhibit very stable trivalency; in fact element 96 should exhibit the trivalent state almost conclusively because, with its seven 5*f* electrons, it should have a stable electron structure analogous to that of gadolinium with its seven 4*f* electrons. As a matter of fact Cm (96) has been found to exhibit only trivalency. The electronic structure of the two groups of rare earths are shown in parallel columns in Table 4.

TABLE 4

Electron Composition of Typical Levels

$_{57}$La	$5d6s^2$	$_{89}$Ac	$6d7s^2$
$_{58}$Ce	$5d^26s^2$ / $4f5d6s^2$	$_{90}$Th	$6d^27s^2$ / $5f6d7s^2$
$_{59}$Pr	$4f^35d6s^2$	$_{91}$Pa	$5f^26d7s^2$
$_{60}$Nd	$4f^45d6s^2$	$_{92}$U	$5f^36d7s^2$
61	$4f^55d6s^2$	$_{93}$Np	$5f^46d7s^2$
$_{62}$Sm	$4f^65d6s^2$	$_{94}$Pu	$5f^66d7s^2$
$_{63}$Eu	$4f^75d6s^2$	$_{95}$Am	$5f^76d7s^2$
$_{64}$Gd	$4f^75d6s^2$	$_{96}$Cm	$5f^76d7s^2$

All the arguments in favor of treating elements from actinium upwards as members of the actinide series have not

yet been published by the author but he is careful enough to add that, in the case of some of the elements in the series, it may be something of an academic matter to assign electrons in the 5*f* or 6*d* shells, as the energy necessary for the shift from one shell to the other may be within the range of chemical binding energies. The electron configuration may differ from compound to compound of an element or even with the physical state of a given compound. This shifting of electron configuration would probably be most pronounced with the middle members of the first half of the series, that is, with uranium, neptunium, and plutonium. Since the energy difference between the 5*f* and 6*d* shells is rather small and since the resonance effects should be rather large, the latter may predominate in determining which energy level lies lowest.

From what has been stated it is clear that similarity of transuranium elements to uranium cannot be explained by any hypothesis other than that of a 5*f* filling up, and the stable trivalent state of Cm (96) indicates that the first 5*f* electron occurs at thorium; as a result, analogous to the lanthanides at the third group of the periodic table, an actinide series makes its appearance. Variable valency that has been observed in the actinide group does not however stand in the way of our consideration of regarding them as a group of rare earths analogous to the lanthanides. In the transition metals, the variability of valency arises from the existence of alternative electronic configurations which differ very little in energy. Such an alternative structure (either a 6*d* or 5*f* transition) for elements from actinium upwards was put forth by M. N. and N. K. Saha in their well-known treatise on modern physics (*43*) long before the discovery of the transuranium elements. In their treatment the authors were certainly guided by their physical sense alone.

From the facts stated above, it is seen that the difficulties that are encountered in finding a suitable place in the periodic table for the lanthanides also occur for the actinide series.

From various considerations the fourteen members of the lanthanide group have been treated as a single element and placed in one place, together with lanthanum, in the third group of the periodic table. In the actinide series too, only thorium and protoactinium have some resemblance to $_{72}$Hf and $_{73}$Ta, respectively, whereas others have properties entirely different from corresponding members of the previous series; the whole series from actinium upwards should be placed with actinium in one place in the third group of the periodic table.

Thorium, protoactinium and uranium may now be taken away from positions previously assigned to them and shown to belong to the third group of the periodic table. The positions of these elements as higher homologues of Hf, Ta, and W were not, however, well defined. Thorium oxide is basic whereas hafnium oxide is amphoteric, tantalum and tungsten oxides are acidic whereas oxides of protoactinium and uranium are basic. Coprecipitation of protoactinium with zirconium as phosphate and with thorium as oxalate is an indication of the tetravalency of protoactinium. Uranium in its tetravalency forms an important class of uranous compounds, and some of its tetravalent compounds display isomorphism with those of thorium. Isomorphism of ThO_2 with UO_2 may serve as an example in point. The crystal structure of uranium shows similarity to that of neodymium, the corresponding member of the lanthanide series. Neodymium crystallizes in hexagonal close packed form, whereas uranium has a distorted hexagonal close packed structure. According to van Heel, uranium is the only element other than the rare earths,

whose compounds exhibit line absorption spectra. In hexavalent state, however, uranium shows little tendency to form simple metallic salts, since UF_6 is the only compound of this sort known. All other hexavalent uranium compounds are oxygenated. Thorium, the first member of the second rare earth series, forms a well-defined group of compounds isomorphous with tetravalent compounds of cerium, the corresponding member of the lanthanides.

In case of lanthanides the electrons penetrate into the 4*f* level, whereas even with the increase of nuclear charge, the outermost shell remains unaltered; consequently there is a gradual contraction of atomic volume because of increasing strength of the binding force of the valence electrons. This is known as lanthanide contraction of Goldschmidt. If a second rare earth series starts with actinium there must be a similar gradual contraction of the atomic volume with rise in atomic number. The ionic radii of tetravalent thorium and uranium in Angstrom units are 1.10 and 1.05, respectively. The lower value in the case of U IV is significant evidence for an analogous actinide contraction which should be due to the penetration of electrons into the 5*f* level.

Further, variable valency is also observed among the lanthanides. Cerium is a typical tetravalent lanthanide. Penta- and even hexavalencies of this element have also been claimed. Tetravalency has been claimed for Pr, Nd, Tb, and Dy. The salts of the type RSO_4nH_2O, where *R* stands for Sm, Eu and Yb, are well known.

In consideration of the facts stated above, thorium, uranium and protoactinium are not strangers in group III of orthodox chemistry. In the positions ascribed to them previously they had long been acting as intruders and thus preventing the discovery of their congeners, neptunium (93), plutonium (94), americium (95) and curium (96).

The question naturally arises as to whether the places left vacant in the fourth, fifth and sixth groups of the periodic table by the transference of Th, Pa and U to group III, will remain so. However, one may anticipate that in the course of the synthesis of elements of higher atomic number not only the quota required by the second rare earth series will be filled up at element 103, but also the production of 104 eka-Hf, 105 eka-Ta, 106 eka-W, 107 eka-Re, 108 eka-Os, 109 eka-Ir and 110 eka-Pt with electrons at the 6*d* shell may be possible, and the completion of the abruptly ending seventh period of the periodic table left incomplete by nature is not too distant.

Of the transuranium elements still undiscovered the chemical properties of elements 103 and 104 (eka-Hf) will be very interesting. The element 103, the last member of the actinide group with its fourteen 5*f* electrons, must have a stable structure analogous to Lu and will be stable only in its trivalency, and the element 104, with which the 6*d* transition will open up with the 5*f* shell completely filled up, will be a very close analogue of hafnium. If the two elements are ever synthesized, their properties will be one of the strongest evidences for the conception of elements 89–103 as rare earths. But elements with charge numbers above 100 are expected to be highly unstable and this may be one of the main causes that may hinder their production in the laboratory.

In conclusion it must be pointed out that there are no direct chemical evidences to distinguish between the *f*-type and the *d*-type of electron configurations. Spectroscopic evidence for distinguishing *d*- and *f*-type electrons would be unique and unambiguous, provided the analysis of the line spectrum can be carried out, and electron composition of levels determined, but it is a Herculean task.

The spectroscopic evidences are of two kinds: (1) absorption spectra of compounds in solution and (2) emission spectra of atoms or ions.

Characteristic absorption bands have been reported for elements 58 (cerium) to 70 (ytterbium), inclusive, and for 92 (uranium) but not for 90 (thorium). No reports on such absorption bands in the case of transuranium elements have yet been released.

Such absorption bands however cannot give information on the number of *f*-electrons. The only way to distinguish different types of electron orbits and to determine how many of each are present in an atom is from the study of its characteristic emission spectrum. The analysis of the emission spectra, reveals that the elements from $_{58}$Ce to $_{71}$Lu (inclusive) contain 4*f* electrons as depicted in Table 4. The study of emission spectra in the case of thorium indicates that there is no such electronic configuration in the element but recent spectroscopic study of U by Kiess, Humphreys and Laun (*48*) reveals that uranium atoms or ions contain three 5*f* electrons as a minimum. The preferred oxidation state VI of $_{92}$U is interpreted to mean that, in this case, three 5*f*, one (or two) 6*d*, and two (or one) 6*s* electrons contribute equally to valence bonds, and the gradual shift in oxidation state VI to III with higher atomic numbers is simply explained by the increase in stability of the 5*f* group as this shell approaches a condition of being half filled.

The fact that thorium does not contain any 5*f* electron (as far as spectroscopic study is concerned) may lead one to anticipate that the outer electronic shell structure of thorium ($6d^27s^2$ or $6d^27s$) is retained in the second rare earth series and the second rare earth series starts from $_{91}$Pa. Protoactinium will then have a $5f6d^27s^2$ or a $5fd^27s$ configuration. The hypothesis can explain the stable tetravalent state of $_{93}$Np and $_{94}$Pu without affecting the 5*f* electron but in order to explain the stable trivalent state of $_{96}$Cm we must take it for granted that one of the *d* electrons does not figure as valency electron. But such stable retention of *d* electrons at the beginning is an unusual phenomenon and spectroscopic evidence that U contains three 5*f* electrons cannot be explained because $6d^27s^2$ outer arrangement permits two 5*f* electrons for uranium.

* * *

In the preparation of this report and those following, the writer has gathered facts freely from papers and reports published in various scientific journals. Most of the diagrams have been reproduced from the originals published in these journals. The writer wishes to acknowledge his indebtedness to the authors of those papers.

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"American research cannot succeed unless the blanket of atomic secrecy is reduced to a minimum and scientists and engineers are allowed to share in the administration of the security system . . . Although the technical engineering details of atomic weapons must be kept secret, scientists can achieve almost nothing without discussing their work with each other . . . Research is a collaborative affair . . . The fundamental facts of nuclear science, the information that is in the realm of pure scientific research, should be open to free discussion. The properties of uranium, for example, could be discussed without revealing the secrets of the atomic bomb."

"Such a scheme would require continual revision with the active cooperation of all responsible engineers and scientists in the field . . . The future generation of atomic scientists is not being adequately recruited or trained, because secret regulations restrict universities to courses in nuclear physics that are more out-of-date now than they were at the beginning of the war."

—*Philip M. Morse,* New York Herald Tribune, *October 20, 1948*

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Ion-Exchangers to Separate, Concentrate and Purify Small Amounts of Ions*

Discussion of apparatus and methods for applying the complex-elution techniques to the preparation of pure solutions of the individual fission products in large quantities for biological and chemical investigations

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ALTHOUGH the phenomenon of ion-exchange,† originally discovered in naturally occurring soils and sands, has been known for a relatively long period and although it has even been exploited industrially for water demineralization and in the laboratory for simple metatheses, it remained for the needs of the Plutonium Project‡ to set the stage for a striking development of this classic procedure in the direction of fine and precise ionic separations.§ This development, linking complex formation and ion-exchange (*1*), has made it possible to separate, with relative ease, accuracy and speed, individual rare earths (*2*) and trace amounts of radioelements from their respective mixtures; it is probably most dramatically illustrated by the separation, within the short time-span required, of the radioactive rare-earth species created in trace amount by nuclear bombardment (*3*) and in the preparation of macroscopic amounts of pure element 61 (*4*). The possible extensions of the basic technique to other difficult separations, to radiochemical investigations, to preparation of very pure species, and to analytical methods are infinite and will occupy the attention of investigators in many fields for some time to come.

The initial explorations and developments of the new application of ion-exchange to ionic separations have been set forth previously by the various investigators involved (*1–4*) and no attempt to review the literature will be made here. The sole purpose of this paper is to give some of the practical details evolved in the adaptation of the complex-elution technique, once discovered, to the problem which inspired the development, that of preparing pure solutions of the individual fission products in large quantities for biological

* The work reported in this paper was done at Clinton Laboratories (now the Oak Ridge National Laboratory), a part of the Plutonium Project, between September, 1944, and June, 1945, under Contract No. W-7405-eng-39 for the Manhattan District. The information will appear in Division IV of the National Nuclear Energy Series as part of the contribution of Clinton Laboratories.

† For a detailed discussion of ion-exchange and its laboratory uses, reference is made to "Laboratory Applications of Ion-Exchange Techniques," by E. R. Tompkins, available upon request from the Isotopes Division, U. S. Atomic Energy Commission, Oak Ridge, Tenn.

‡ Twelve papers from the Plutonium Project and three others, which appeared as a Symposium on Ion-Exchange in the November, 1947, *J. Am. Chem. Soc.*, are available as a single reprint for $0.35 from the American Chemical Society, 1155 16th Street, N. W., Washington 6, D. C.

§ The production of synthetic, higher-capacity, ionically strong, chemically resistant ion-exchangers should also be mentioned as a critical contribution to this development.

and chemical investigations. Although these details follow almost automatically from the principles of ion-exchange, their usefulness for separations in general and high-level radiochemical ones in particular seems to warrant a separate exposition. It is worth noting that the apparatus and methods to be described, modified and improved, are used to prepare the fission products currently being distributed by the Oak Ridge National Laboratory (*5*).

General Chemical Features

The basic chemical operations are two—adsorption and desorption (elution). Repeated under varying conditions as often as necessary, these steps make it possible first to separate the desired constituent and then to concentrate and metathesize it to the final form. The separation will usually begin by allowing a solution, containing the cations which it is desired to separate from each other, to flow through a cylindrical bed of the cation-exchanger that has previously been converted to, say, the hydrogen form by treatment with acid. The rates and amounts will be chosen so as to confine the adsorbed cations to the topmost fraction of the bed; these factors will obviously be functions of the capacity of the exchanger in relation to the amount of cation to be handled, the affinities of the cations (including those which they replace) for the exchanger and the rates at which they react with it (these being influenced by particle size and temperature).

Once adsorbed, elution is commenced with a solution which will displace one cation to a greater degree or at a faster rate than any of the others. The continued flow of this eluting solution through the column will develop "bands," as in the classical chromatographic separations (*6*, *7*), as a result of which the most easily displaced cation will arrive at the bottom of the column before the others and thus be separated from them. Concentration and metathesis are simply repetitions of these two steps without the necessity of using only a fraction of the bed (since length of column is no longer of critical importance) and with the composition of the eluting solution being all-important.

Obviously, the separation of two constituents by such a method depends upon finding an eluting reagent which will give different values of the respective distribution coefficients. If the affinity of each constituent for the exchanger varies sufficiently from the others, the separation can be accomplished solely by simple ion-replacement with acid or salt solutions. When this is not the case, it is necessary to seek an eluting agent which will magnify what differences do exist or create new ones. It was the use of complex-forming reagents (citrates, tartrates, oxalates) which, because of the variation in the dissociation constants of the complexes formed by them with the ions in question, gave differences in the distribution of the fission products and rare earths between exchanger and solution sufficient to permit the striking separations already reported (*1–4*).

The complex formed by a polybasic acid with a polyvalent cation is dependent upon *p*H, which determines the concentrations of the various anions of the acid. Thus it is possible to decompose such complexes by simple addition of acid, freeing the cation and rendering it more adsorbable by the exchanger. This affords the means for concentration and metathesis steps; the eluting solution containing a cation as a complex ion is acidified and allowed to flow through another exchanger bed, whereupon the cation is removed from the solution. From this second bed it can be released by a greater variety of reagents, because separation from like elements is no longer required.

Experimental

1. Separation of Species

a) *Apparatus for High-level Separations.* The essentials of remotely controlled radioisotope separation are met by the apparatus (Fig. 1), which was constructed in September, 1944, as follows:

1) Resin is slurried into the funnel (7) at the top of the cell and settles into the column (3) through the large stopcock (8), coming to rest upon a sintered disk at the bottom of the column.
2) Gravity flow of active throughput is achieved by drawing (12, 13) the solution from a storage bottle (20) into a burette (6) above the column. From here it is allowed to run through the column, the rate being observed through a periscope by the markings on the burette and being controlled by a stainless steel needle valve (4). As a safety device, to prevent the column from running dry, a close-fitting float valve is included in the burette (5).
3) Washing and eluting solutions can be introduced either through the burette used for the active throughput or, since they are not radioactive at the start, through a burette mounted on the outside of the shielding (10). Rate is controlled by stopcocks, a dropping device being inserted in the line to permit easy observation.
4) An ionization chamber (16), connected (15) through a Beckman amplifier to a Micromax recording milliammeter, permits the continuous observation and recording of the radioactivity of an eluate in terms of relative ionization through the 25 mg/cm² glass wall of the ionization chamber. This reading is obtained several minutes before the eluate reaches the switching device (19) ["selector funnel" (2)] and is diverted to storage bottles (1) or the drain (21), since the volume of the line connecting chamber and selector is about 10 ml and the flow rates are 1–5 ml/min.
5) Since the glass tube containing the resin is too narrow to allow backwashing *in situ*, a large vessel (9) permitting suspension of the resin is located directly above the column and connected to it by the large-bore stopcock. An overflow from this vessel to the drain allows the resin to be washed out of the system completely by increasing the backwash flow rate (this can be assisted through the outside burette line).
6) Samples of the eluate are taken from a tube below the ionization chamber assembly (17, 18).

b) *Solutions and Ion-Exchanger Used.* All of the work reported was done with the synthetic cation-exchanger Amberlite IR-1 (*8*) [although many other varieties of cation-exchanging material may be used (*2*, *3*)], ground and screened to furnish material of 40–60 mesh. After slurrying the resin into the column, it was washed exhaustively with 3 *N* HCl to convert it into the hydrogen form, which was known to adsorb the several species of interest to us.

The fission-product mixture, from which the initial radiochemical separation was made, consisted of a dilute ($\sim$ 0.1 *N*) HCl solution which contained, besides the radioactive (and stable) fission-produced nuclei discussed below, varying amounts of ionic impurities originating at various points in the past history of the starting solutions. Fe, NH_4^+ and NO_3^- were usually removed from the fission-product mixture before the resin adsorption step, Fe by isopropyl ether extraction and NH_4^+ and NO_3^- by HCl evaporation. The Ru and Te present appeared nearly quantitatively in the effluent from the adsorption step and could be recovered from it by special methods. Eight-day iodine was not present in appreciable amounts in the 30 to 90-day-old fission material used in these separations.

The complex-forming eluting solutions used (oxalic acid, tartrate and citrate) were made by dissolving the crystalline acids in water, diluting to the proper concentration, and then converting the resultant acid solutions

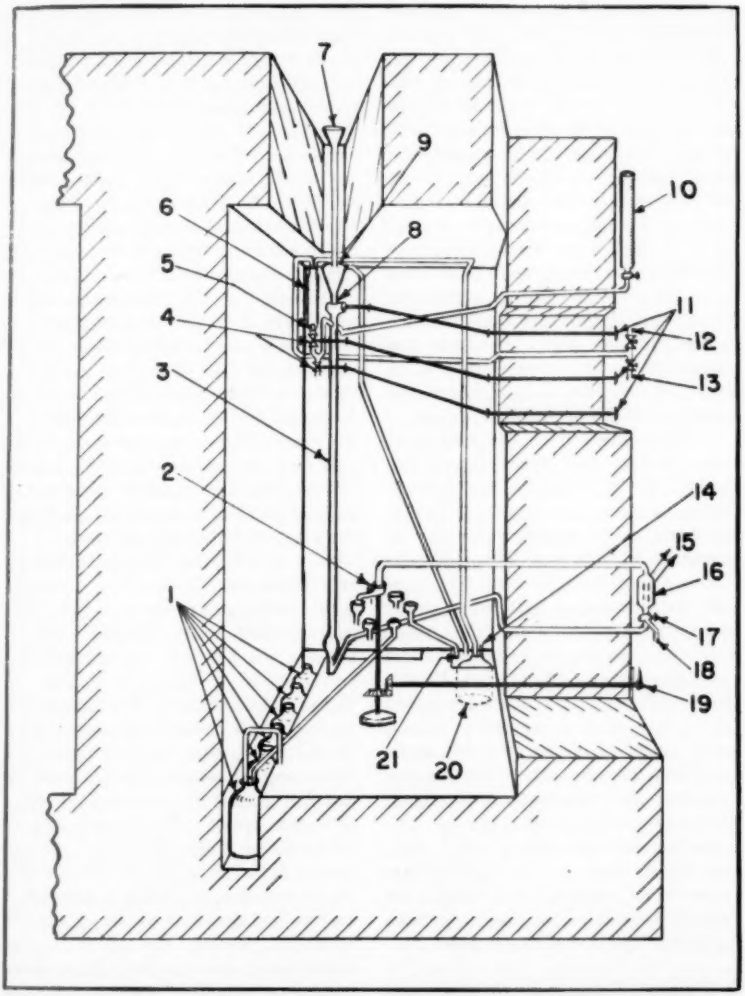

FIG. 1. Remotely controlled, shielded ion-exchange apparatus for curie-level separations, installed in hot laboratory at Oak Ridge National Laboratory (part of two-foot concrete wall and other fixtures cut away to show operation)

1. Storage bottles for final fractions (each attached to a separate funnel)
2. Rotating "selector" funnel
3. Ion-exchange column
4. Stainless steel needle valves
5. Ball check valve
6. Burette for measuring "hot" influent solutions
7. Funnel for introducing resin
8. Large-bore stopcock
9. Reservoir for suspending resin
10. External burette for "cold" solutions
11. External handles controlling 8 and 4
12, 13. External air and vacuum connections
14. Line for introducing solutions into 20
15. Electrical leads to amplifier and recording milliammeter
16. Flow-through ionization chamber
17. Flow-rate control and sampling valve
18. Sampling and backwash tube
19. Selector funnel (2) control
20. Storage bottle for "hot" solution
21. "Hot" drain, to waste storage tanks (at bottom of recess)

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to the desired *p*H values with concentrated NH_4OH.

c) *Operation.* The volume of the column described is about 100 ml and such a column of Amberlite IR-1 resin absorbs practically quantitatively the cationic fission products associated with many grams of cationic impurities. In practice, since chromatographic specificity is known to depend to an appreciable degree on top-of-the-column adsorption, we kept well below this figure (in most of the reported work, below $\sim$ 0.1 gram). The total ionic strength of the throughput was due principally to H^+, always present in about 0.1 *M* concentration to prevent adsorption of active species on glass.

The separation of the individual active species was accomplished (see *Results*) by the use of the specific eluting reagents described earlier (*1*) which depend for their action upon the formation of complex ions with the adsorbed cations. Zr and Cb were first eluted together with 0.5% oxalic acid (sometimes followed by 7% oxalic acid to insure complete removal). The trivalent elements (Y, 61, Nd, Pr and Ce) were then eluted in the order named by 5% citric acid or tartaric acid, converted with NH_4OH to *p*H values in the range 2.7–3.3; the *p*H of the influent was kept at or near the lower figure until most of the leading element (Y) was removed before being raised, stepwise or at once, to the higher value required to remove Ce. Finally, Sr and Ba were eluted in that order with 5% citrate converted to *p*H 5–6.

2. Volume Reduction. The eluates from the radiochemical fractionations on a column of the size described contained (see *Results*) the active species, as their complex ions, in volumes of several hundred ml of the eluting solution. Concentration of each active species was achieved by re-adsorption upon a smaller column [*cf.* Fig. 1 of ref. (*1*)] after decomposition of the complex ion.

The experiments previously presented indicate that Ce is not eluted appreciably from Amberlite IR-1 by 5% citrate at $pH < 2.80$, nor is Y by 5% citrate at $pH < 2.0$. Sr and Ba are not eluted appreciably by 5% citrate at $pH < 4.0$. There must be minimum concentrations of certain citrate anions in the solution for elution to occur, and these concentrations are markedly dependent on *p*H. Hence, an eluate containing Y^*, for example, in 5% citrate at a *p*H of 2.8 should lose the Y^* to Amberlite IR-1 resin if the *p*H of the eluate (now the influent) is lowered to 2.3 or 2.0 before throughout. Such is the case, and the re-adsorption of the various trivalent ions is easily accomplished by the addition of a small amount of HCl to the eluate, lowering the *p*H (of 5% citrate) to 2 or less.

In principle, this applies to the divalent ions as well, but here a complicating factor enters, namely, the NH_4^+ concentration. The NH_4^+ in 5% citrate at *p*H 5.0 is of considerable importance in Sr and Ba elution [*cf.* Fig. 4 of ref. (*1*)]. Acidifying such an eluate, which destroys the complexing anion, Cit^{-3}, does not diminish the NH_4^+ concentration. In this case, in order to achieve a reasonable degree of re-adsorption, it is necessary, in addition, to dilute the NH_4^+ concentration into insignificance (< 0.1 *M*). When this is done, giving a solution of Ba^* in $< 1\%$ citrate at $pH < 3.5$, the resin will absorb the divalent ions rapidly and quantitatively from large volumes of solution. For example, the Ba^* from a volume of about 400 ml of such a solution (40 ml of 5% citrate at *p*H 6.0 diluted and acidified to 400 ml of ½% citrate at *p*H 2.5) was adsorbed by a 2-ml IR-1 column 1 cm^2 in area, in 20–80 minutes with a loss of less than 10%. This Ba^* had been eluted previously from a 20-ml column of the

same diameter in 40 ml of 5% citrate at *p*H 6.0 and was subsequently eluted from the 2-ml column in about 4 ml of the same reagent. The cycle of elution, dilution, acidification, re-adsorption (on a 10-fold smaller column), and re-elution, therefore, netted a concentration of 10-fold with respect to Ba*.

In the case of Y, Ce and other species which are less affected by 0.5–0.7 *M* NH_4^+ than are Ba and Sr, dilution before re-adsorption is not necessary; hence, simple acidification, followed by re-adsorption and re-elution, may give volume reduction factors on the order of 100 per cycle. Zr and Cb, because of their radiocolloidal propensities, may show even greater volume reduction factors, but this has not been tested. Preliminary experiments show that Cb, if eluted by 10% citric acid (*p*H $\sim$ 1.8), may be re-adsorbed after acidification of the citric acid solution to *p*H $\sim$ 0. Zr, which can be eluted by 5% citrate at *p*H 2.4, may be re-adsorbed at a *p*H < 1.8. In these experiments a volume reduction factor of 10 was achieved.

3. Removal of Chemical Impurities from a Carrier-Free Fission Product Solution. In the starting solutions used there were cationic impurities to be dealt with, on the order of 100 mg Fe, 10 mg each of Cu, Ni, Cr, Mn, Ca, Mg, Zr, Na and K, and 1 mg or less of Pb, Ti and V. Each of these is adsorbed more or less quantitatively by the resin during the throughput and appears in one or another eluate as the fractionation procedure progresses. Since the criterion for determining which fractions of the eluate to collect was its radioactivity, it was not known in advance in which fractions these inactive impurities would appear. One could, of course, study each impurity independently and, with information as to its column behavior, arrange the elution procedure so as to separate it; however, in view of the success of an empirical procedure introduced into the volume reduction step, it was not necessary to conduct such an investigation in order to achieve the desired results.

The procedure used is based upon the principle that each ion has a specific affinity for IR-1 with regard to its replaceability by a bulk cation (*9*), H^+ in the present case. The solutions to be concentrated and purified were, however, the end-products of a citrate-complexing fractionation which may or may not have any relationship to the order of replaceability by H^+ alone; hence, the impurities in a given fraction may be easily separable from the chief radioisotopes of that fraction by simple ion-replacement alone.

The citrate eluate was therefore acidified and adsorbed on a smaller (10-ml) IR-1 column, as described above. A simple water wash removed all adherent citrate. Then HCl, starting with 0.1 *N* and going up stepwise to 0.5 or 1 *N*, was passed through the column. This caused a progressive elution of all those cations, including NH_4^+, which were less strongly adsorbed than the radioelement desired. Finally, this element appeared in the eluate and was detected because of its radioactivity. The influent was then changed to 3 *N* HCl and all of the radioelement removed in a small volume of this solvent. After the effluent radioactivity had fallen to a sufficiently low value, the collection was terminated and the solution examined for its solid content by evaporation and weighing. If this was still too high, the adsorption-washing-elution cycle was repeated. Usually one or at most two such cycles sufficed to reduce the total solids to a few milligrams (*cf.* Table 1) beyond which it is practically impossible to go, for the weight of the chlorides of isotopic impurities and of the active and inactive fission-bred isotopes is of this order [*cf.* Table 1 of ref. (*1*)].

When the character of the impurity was known, specific washes were used prior to the HCl procedure. Cu, usually found in the Y fraction, was eluted with NH_4OH-NH_4Cl mixture; Ca was found to precede Sr in a citrate elution just as Sr precedes Ba and Ba precedes Ra (*10*). In general, the HCl washing is capable of removing all contaminants usually encountered. Al, when present, appeared in the Y fractions and was the most difficult impurity to remove, yielding only after several cycles.

4. Metathesis. It will be noted that the last step in the purification procedure resulted in the metathesis of the radioelement and the change of its solvent from citrate to chloride. It is obvious that any anion may be eliminated simply by adsorbing the cation on an acid resin, washing out the residual anion as its acid, and desorbing the cation with the acid form of a desired anion.

5. Very Pure Radiochemical Species. If, as described above, a re-adsorption-elution cycle is used for chemical purification of a radioactive species, it is possible to introduce into it one or more radiochemical purification steps. Consider, as an example, a Ce* fraction containing, in addition to solid impurities, Y* to the extent of 5% of the gross activity. Immediately after re-adsorption, one may wash the resin exhaustively with 5% citrate at $pH \sim 2.8$, just as in the preceding fractionation step, until Ce* begins to appear in the eluate. If each such cycle removes 95% of the Y*, successive cycles will result in the Y* contamination being reduced to 0.25%, 0.0125%, etc., of the Ce* (some Ce* will, of course, be lost in the Y* cuts) so that any required degree of radiochemical purity can ultimately be achieved (*3*).

Results

The results of three typical early "production" runs (made in 1944 and 1945) are given to illustrate the application of the above methods. The analytical results presented were obtained by "standard" radiochemical analysis. A word with regard to the state of such analyses during the period of this work is in order.

Although the methods for determining Y* and Ce* in their mixtures were quite reliable when both contributed significantly to the total activity, they did not allow (at the time this work was done) an accurate analysis of $\sim 1\%$ of Y* in Ce* and vice versa, particularly when there were significant amounts of Pr*, Nd*, etc., present. [It may also be noted that certain of the radioisotopes in our solutions had not been identified at the time this work was begun; indeed, isolation and identification of Nd^{147} and 61^{147} were first made in certain of our fractions (*4*)]. In several cases, the expenditure of considerable additional effort on the analysis of certain fractions resulted in significant diminution of the extent of cross-contamination first reported. Hence, the analytical results can be relied upon only to indicate the maximum degree of cross-contamination.

The first curie-scale fission-product separation (September, 1944) is summarized in Fig. 2, which is a copy of the automatically recorded ionization current observed [*cf.*, Fig. 1; 15 and 16] during the run itself. The numbers along the abscissa represent the volume of a particular eluting agent used up to the point in question; those on the ordinate are proportional to the ionization current measured. The vertical lines indicate the beginnings and ends of specific fraction, taken by means of the selector funnel (Fig. 1; 2 and 19).

The specificity of the method is indicated by the analyses given (the limitations of which have been men-

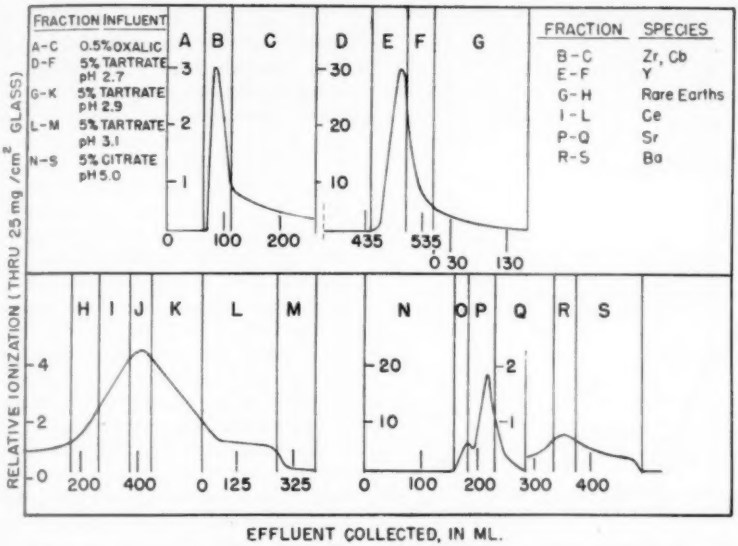

FIG. 2. Separation of fission products by complexing elution (D9, 9/5/44)
Resin: Amberlite IR-1, 40–60 mesh, acid form
Bed: 1 cm² × 100 cm
Rate: 1–2 ml/cm² min

		Effluent			
Fraction	*Influent*	*ml*	*mc*	*Species**	*Radioactive impurities*
A	0.5% oxalic acid	70	~0	...	...
B	"	45	190	Zr, Cb	(none)
C	"	150	190	Zr, Cb	(none)
D	5% tartrate, *p*H 2.7	445	4	...	...
E	"	60	225	Y	~5% R.E.
F	"	50	230	Y	"
G	5% tartrate, *p*H 2.9	165	135	Y	3% Ce, 47% R.E.
H	"	105	75	R.E.	15% Y, 30% Ce
I	"	120	160	Ce	25% R.E.
J	"	60	100	Ce	6% R.E.
K	"	130	180	Ce	< 1%
L	5% tartrate, *p*H 3.1	260	120	Ce	< 1%
M	"	140	65	Ce	3% Sr
N	5% citrate, *p*H 5.0	160	0	...	...
O	"	23	12.5	Y^{90}, La^{140}	< 10%
P	"	45	257	Sr	< 1%
Q	"	108	240	Sr	6% Ba
R	"	36	56	Ba	< 1% Sr
S	"	105	96	Ba	< 1% Sr

* Exclusive of short-lived daughters (*e.g.*, Y^{90}, La^{140})

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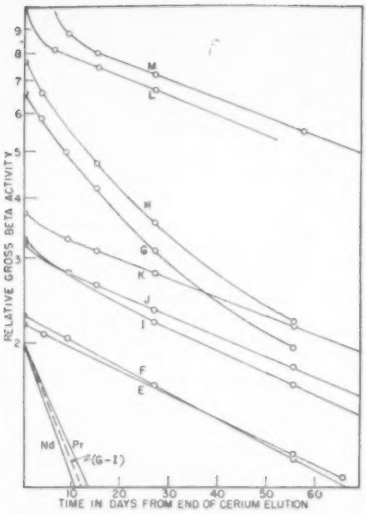

FIG. 3. Decay curves of fractions from run D9 (see Fig. 2), showing presence of short-lived rare earths between Y and Ce fractions (see text)

tioned above). Some interest is attached to the fraction *O*, containing a small amount of activity preceding the Sr fractions (*P*, *Q*) and Ba fractions (*R*, *S*); upon analysis, this activity proved to be due almost exclusively to 60-hour Y^{90} and 40-hour La^{140}, daughters of Sr^{90} and Ba^{140}, respectively, which had grown from their parents during the overnight shutdown of the column (between *M* and *N*) and which were eluted ahead of the Sr and Ba fractions, as might have been expected, by the more alkaline citrate solution. (This represents a simple procedure for periodic "milking" of La^{140} and Y^{90} from their parents). That such behavior was not anticipated at the time of the work is in keeping with the dearth of information then available; neither the rare-earth separations (*1*, *2*, *3*, *4*) nor the Sr-Ba separation achieved in this run were expected.

The presence of rare-earth radioelements or elements other than Y and Ce in fractions *G* and *H*, suspected by Marinsky and the authors, was immediately apparent from decay curves (Fig. 3) run by Cohn on fractions *E* to *M*, inclusive. Whereas the yttrium fractions (*E*, *F*) and cerium fractions (*I*, *J*, *K*, *L*, *M*) show the long half-lives characteristic of Y^{91}, Ce^{141} and Ce^{144}, the intermediate fractions betray the presence of an activity having a period of about 12 days. Since Pr^{143} has a 14-day and Nd^{147} [then unknown but being traced and eventually identified chemically by Marinsky (*4*) in the same fractions] an 11-day period, the average of 12 days is now to be expected.

Two subsequent production runs are similarly recorded in Figs. 4 and 5. D13 (Fig. 4) shows more clearly the relationship of *p*H to the Y-rare-earth-Ce fractionation (citrate was used here instead of tartrate) and the relative time scale of the elution sequence. The anionic (Ru^*, Te^*) breakthrough during the initial throughput is also shown. D14 (Fig. 5) presents the complete picture of a fission-mixture fractionation, showing the tendency of Sr to "leak" into the last Ce fractions if the Ce is eluted at high *p*H (high NH_4^+ concentration). The fact that the rare-earth fractions in both cases are about half Y and Ce can be explained on two counts: (1) the age of the material (Nd^* and Pr^* have short half-lives and hence existed in low amounts in the starting mixtures), and (2) the fact that cuts were deliberately arranged so as to procure the maximum early yield of Y and Ce for the biological experiments in which these isotopes were to be used.

Following the radiochemical separations demonstrated in Figs. 2, 4, and 5, those fractions which were to be concentrated, purified and metathesized to the required form were acidified and re-adsorbed on the smaller (10-ml)

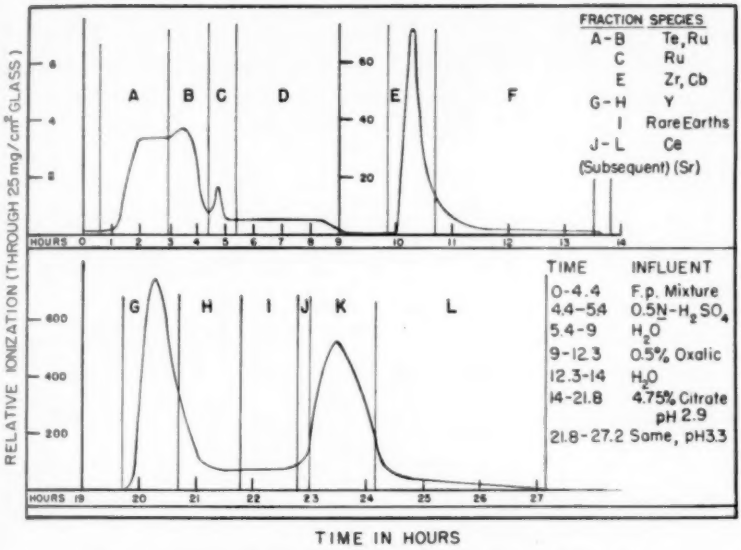

FIG. 4. Separation of fission products by complexing elution (D13)
Resin: Amberlite IR-1, 40–60 mesh, acid form
Bed: 1 cm² × 100 cm
Rate: 1–2 ml./cm² min

Hours	*Influent*	*Fraction*	*Effluent Cut* (*ml*)	(*mc*)	*Species*	*Radioactive Impurities*
0–2.9	Fission products	*A*	200	100	Te, Ru	~ 20% (traces Cs, Sr)
2.9–4.4	Water	*B*	400			
4.4–5.4	0.25 *M* H_2SO_4	*C*	100	...	Ru	< 2%
5.4–9	Water	*D*	...	...	...	...
9–12.3	0.5% Oxalic	*E*	35	400	Zr, Cb	< ½% R.E., Sr, Ba
12.3–14	Water	*F*	200	...	...	...
14–21.8	4.75% Citrate *p*H 2.9	*G*	90	700	Y	< 1% Ce, Sr
		H	150	200	Y	18% Ce, 0.2% Sr
21.8–27.2	4.75% Citrate *p*H 3.3	*I*	120	120	Ce	34% R.E., 3% Y
		J	30	30	Ce	< 30% R.E., Y
		K	130	700	Ce	< 2% Y, 0.1% Sr
		L	370	210	Ce	< 2% Y, 0.2% Sr
		(Left on column: 700 mc Sr)				

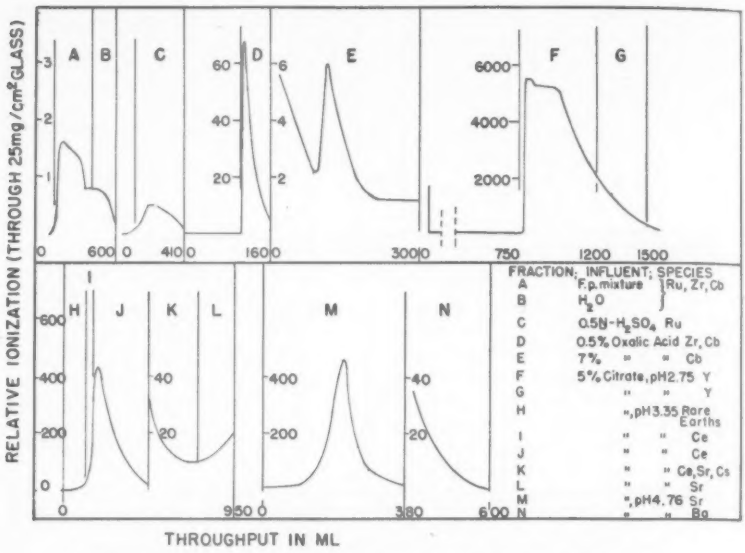

FIG. 5. Separation of fission products by complexing elution (D14)
Resin: Amberlite IR-1, 40–60 mesh, acid form.
Bed: 1 cm² × 100 cm
Rate: 1–2 ml/cm² min

Influent	*Fraction*	*Effluent Cut* (*ml*)	(*mc*)	*Species*	*Radioactive impurities*
600 ml Fission mixture, (free of U and Pu)	*A*, *B*	520	120	Zr, Cb	22% Ru, 15% misc.
410 ml 0.5 *N* H_2SO_2	*C*	...	...	Ru	Te, Cs
160 ml 0.5% oxalic acid	*D*	60	600	Zr, Cb	(none)
300 ml 7% oxalic acid	*E*	300	...	Cb, Zr	...
1,500 ml 5% citrate, *p*H 2.75	*F*	400	1060	Y	1% Ce, < 1% Sr
	G	265	245	Y	2% Ce, < 1% Sr
950 ml 5% citrate, *p*H 3.35	*H*	300	100	R.E.	40% Y, 4% Ce, 1% S
	I	35	...	Ce	...
	J	315	880	Ce	2% Y, < 1% Sr
	K	250	75	Ce	14% Sr (Y, Cs)
	L	200	71	Sr	16% Ce
600 ml 5% citrate, *p*H 4.75	*M*	380	930	Sr	7% Ba, 1% Ce
	N	220	110	Ba	2% Sr, < 1% Ce

TABLE 1

Sample Results of Concentration, Purification, and Metathesis by Re-adsorption on Amberlite IR-1 of Fission-Product Solutions Separated by Complex Elution

			(a) *Original*			(b) *Final*			
Sample	*Major isotope*	*Radiochemical impurities*	*Amt. (mc)*	*Vol. (ml)*	*Solvent*	*Amt. (mc)*	*Vol. (ml)*	*Solvent*	*Weighed solids (mg)*
D9-Q	Sr	6% Ba	240	108	5% Cit	150	25	1 *N* HCl	< 5
D9-I, K	Ce	~ 10% Y + Pr	350	250	5% Tart	300	"	"	3½
D9-F	Y	< 5% Pr, R.E.*	230	50	5% Tart	200	"	"	< 1
D13-L	Ce	< 2% Y, 0.2% Sr	210	370	5% Cit	175	"	"	< 1
D13-K	Ce	< 2% Y	700	130	5% Cit	(~ 600)	"	"	3–5
D14-F	Y	1% Ce, 0.7% Sr	1060	400	5% Cit	800	"	"	1

*Rare earth

columns. After washing with water, the removal of solids and (if needed) further radiochemical purification was carried out by washing with the reagents mentioned above. The success of this procedure is shown by the figures in Table 1, listing the composition of certain fractions, (*a*) as received from the first column, and (*b*) as shipped after 1 or 2 recyclings through the smaller columns.

Summary

Ion-exchange procedures are described for separating, concentrating, purifying and metathesizing radioactive cationic fission products to recover them in forms and purities suitable for biological or other experimentation. The essential steps are:

1) Adsorption at the top of an ion-exchange column
2) Elution of each species separately by complex formation
3) Re-adsorption, following complex destruction by simple acidification, on smaller columns
4) Purification from radioactive and stable contaminants and elution in the desired solvent by suitable choice of reagents and one or more recyclings on the smaller columns.

Application of the method, of which examples are given, has yielded 100–1,000 mc amounts of the major fission species in radiochemical purities of > 95–98% and associated with <1–5 mg of total solids, whereas the original solutions contained on the order of 100 times this amount.

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Radioisotopes in Nutritional Trace Element Studies—III

Copper, molybdenum, and zinc as they affect plant and animal nutritional diseases are discussed in this last of a series of three papers on trace elements for study of metabolism

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THIS CONCLUDING ARTICLE will review experimental investigations based on the use of the radioisotopes of the nutritional trace elements *copper*, *molybdenum* and *zinc*. In discussing the present status of the problem, references will be made only to review or key papers, and recent articles of special interest. The occurrence of mineral nutritional diseases of plants and animals in the United States has been outlined by Beeson (*1*); observations to 1944 on the trace elements as related to animal health have been compiled by Russell (*2*); general reviews on mineral metabolism have been presented in the *Annual Review of Biochemistry* for the years of 1943, 1944 and 1947 (*3*, *4*, *5*).

The Copper Problem

The essentiality of copper in the diet, and the association of this element with a definite function in the animal body has been recognized since the early 1920's. The review of Elvehjem (*6*) may be consulted for the historical development of the knowledge of copper in biology. The copper requirement for the adult human has been placed at one to two mg per day. Naturally occurring copper-deficiency diseases of cattle or sheep have been reported in various parts of the United States, Holland, Finland, Australia and the United Kingdom. The deficiency is usually manifested in livestock, where the copper content of the forage is less than four ppm on the dry basis; horses have not been reported as affected on such pastures, although some of the copper-deficiency symptoms have been observed in foals. The over-all evidence would indicate that ruminants are somewhat more sensitive to copper deficiency than are single-stomached species.

In cattle, the symptoms of copper deficiency are anemia, severe diarrhea, cessation of growth, depigmentation of hair, poor reproduction and abnormalities in bone development. In addition to these symptons, adult sheep exhibit a characteristic alteration in the qualities of the wool growth, which is of great economic importance. It has been established that a serious disease of unweaned lambs known as enzootic ataxia, which is wide spread, particularly in certain parts of Australia, is caused by a deficiency of copper. Apparent copper deficiencies have been reported on pastures well supplied with copper, which would indicate the existence of factors affecting availability or utilization of the element by the animals.

Convenient and reliable chemical analytical methods for copper, with a sensitivity adequate to determine this element in the amounts normally present in the animal tissues, have led to a

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considerable accumulation of data on various aspects of copper metabolism. Elvehjem (*6*), in 1935, presented an extensive review of the biological significance of copper, and Schultze (*7*) comprehensively discussed the role of this element in blood formation on the basis of experimental evidence available to 1940. Typical investigations based on chemical analysis include balance and tissue accumulation experiments with rats (*8, 9*), analysis of blood copper in rabbits and sheep after oral and intravenous administration (*10*), detailed experiments on the excretion of copper by the rabbit (*11*), and a study of liver storage in the rat, rabbit, and guinea pig (*12*).

No clear picture exists, however, of the function of this important element. Copper is not a constituent of the hemoglobin molecule and has not been identified as a necessary component of the structural material of the circulating erythrocyte. There is much evidence that copper facilitates or is essential for utilization of iron by the blood-forming organs and for the mobilization of iron from the tissues. Two copper protein compounds have been isolated, one from the blood and the other from the liver of mammals (*13*). The possible catalytic function of copper has been emphasized by the identification of several enzymes as copper protein compounds. Copper has been found necessary for the formation and maintenance of cytochrome oxidase activity of rat tissues. The observation of bone abnormalities in connection with copper deficiency presents an interesting aspect which has received practically no attention as yet.

Radioisotope Studies with Copper: The most suitable isotope of copper for biological tracer studies is Cu^{64}, with a half-life of 12.8 hours. The radiation characteristics and suitable methods for assay have already been described. Successful use of Cu^{64} in animal experimentation must take into consideration the toxicity of this element and the short half-life of the isotope. This means that the material used should have a high specific activity and that the preparation of the samples for assay should be as rapid as possible. The toxic level depends largely upon the conditions of administration; for instance, a single dose of 5 mg copper as the sulfate injected into the blood stream of the rabbit, or 100 mg given in dilute solution by stomach tube is fatal within a few hours. On the other hand, as much as 200 mg copper dried on the food can be administered to the rabbit every day for months with no observable effects. With sheep and swine 1 to 3 gm doses are used therapeutically, and 4 to 8 gm doses for the bovine.

In 1941, Mazia and Mullins (*14*) reported the use of Cu^{64} in a study of the oligodynamic action of heavy metal ions. The isotope was prepared in the cyclotron with an activity of about 10 mc per gm. Leaves of *Elodea canadensis* were immersed in 10^{-6}, 10^{-8} and 10^{-10} *M* solutions of $Cu^{64}Cl_2$; after a given time of immersion, a known weight of leaf material was washed in 500 volumes of distilled water and analyzed with a a Geiger-Müller counter. No further experimental details were described. It was found that the tissues were able to accumulate considerable copper from a low external concentration; the ratio of Cu^{64} inside the leaf, to the Cu^{64} outside was in the range of 10^4 to 10^5. It was concluded that copper, in extreme dilutions, exerts its physiological effects by virtue of the power of protoplasm to bind ions against a concentration gradient, so that the concentrations present are relatively high.

Yoshikawa, Hahn and Bale (*15*), in 1942, described the use of Cu^{64} to study the uptake of this element by the red blood cells in normal and anemic dogs. Their material was prepared by proton bombardment of nickel, after which the nickel was dissolved in a small amount

of concentrated nitric acid, diluted with distilled water, and 2 mg inert copper added as a carrier. After precipitation with H_2S, the copper was dissolved in a few drops of nitric acid and plated onto platinum from a solution of 1 ml concentrated HNO_3 and 3 ml concentrated H_2SO_4 in 100 ml water. The deposited copper was dissolved in concentrated HNO_3 and after drying on a steam bath the residue was made to 25 ml with water. This solution was mixed with 20 gm dried white bread and 10 gm of salmon for feeding; carrier was added so that 0.8 mg copper as the nitrate was fed to each animal.

Samples were prepared for radioactivity assay by ashing with 5 ml concentrated H_2SO_4, with a little perchloric acid used as needed. Water was added and, using phenol red as an indicator, neutralization with 40% NaOH was carried out. Then weakly acid (yellow), 20 ml of saturated $Na_4P_2O_4$, were added and the solution made just alkaline. After cooling and transferring to a separatory funnel, 30 to 40 ml ethyl ether and 2 ml 0.1% sodium diethyldithiocarbamate were added and the ether layer separated after thorough shaking. The water layer was again extracted with ether after a few hundreths of a milligram of copper were added as carrier. This extraction was repeated three or four times, the extracts combined and evaporated, a few drops of concentrated HNO_3 added, and the solution made to 2 ml. The measurements were made with a dipping-type counter similar to the method described in the first paper of this series.

Following ingestion of radioactive copper by the dog, the metal appeared quickly in the plasma, the concentration reaching its peak in from 2 to 5 hours, after which it fell abruptly. Demonstrable amounts were still present after 2 days. The radioactive copper likewise appeared rapidly in the circulating red blood cells and there was a slow but gradual increase in its concentration over a two-day period. An insufficient number of animals was used to permit a definite conclusion, but there was an indication that where the hematopoietic activity was greater than normal the uptake of the copper by the red blood cells was increased.

In 1942 Schultze and Simmons (*16*) employed Cu^{64} in studies on nutritional anemia of rats. Nickel targets weighing 200 to 250 mg were bombarded with 6.7-Mev protons in the cyclotron for 8 to 12 hours; the copper content of the nickel was about 0.1% so that the sample contained 0.2 to 0.3 mg of copper. The target was dissolved in a mixture of HCl and HNO_3, the solution evaporated, diluted, and repeatedly extracted with a CCl_4 solution of dithizone (0.1 mg of dithizone per ml of CCl_4) until the color of the reagent remained unchanged. The CCl_4 extract was evaporated to dryness, ashed with 0.2 ml of concentrated H_2SO_4 and a few drops of H_2O_2, and then diluted with 0.8 ml of water. The acid was neutralized to phenol red with redistilled ammonia and made to about 2.5 ml. The activity of these samples at time of feeding was about 0.5 millicuries. Of this solution, 1 ml was fed to each rat and 0.1 ml was used as a calibration standard and for chemical determination of total copper. The radioactive material was fed to the rats in a small amount of milk; since the animals were fasted 14 to 16 hours before feeding, rapid consumption resulted, however, any residue left in the feed dish was determined by analysis and corrections applied.

Except for the carcass and different parts of the intestinal tract, the samples were prepared for measurement as follows: the tissues were weighed, transferred to glass-stoppered digestion flasks of about 60-ml capacity, and ashed with sulfuric and perchloric acids. After complete digestion, the acid solution was diluted and neutralized to about

pH 2, with patent blue *V* as indicator. To this solution 3 ml of dithizone in CCl_4 were added and the copper was extracted by mechanical shaking for 15 minutes. A solution of dithizone containing 0.1 mg per ml CCl_4 was used. The CCl_4 layer was used directly for radioactivity measurement. Under these conditions, quantitative recovery was obtained with or without added tissue. Since the feces and intestinal tract contained considerable activity, they were wet-ashed, the ash solutions made to volume and measured directly; this was also done with the carcasses except that they were dry-ashed. Measurements were made with the dipping-type counter as previously described in these articles. In aqueous solutions no corrections were necessary for self-absorption by the solvent; however, with CCl_4 solutions, only 85% of the corresponding activity in aqueous solution was registered in the counter, so that a correction was applied.

Typical results are presented in Table 1. The rather low retention of copper by the animal is well illustrated. There was no explanation for the low total recovery of the administered copper. The iron-deficient rats, which were receiving adequate copper, showed a somewhat lower retention than the copper-deficient group. Of the radiocopper in the whole blood, from 49 to 75% was contributed by the plasma. It was very interesting that per unit weight the kidneys showed 1½ to 3 times more radioactive copper than the liver. It was calculated that the deposition of copper in the bone marrow was about the same order of magnitude as in the liver, and was sufficient to elicit an increase in cytochrome c oxidase activity and to initiate hematopoietic activity. This demonstrated the entrance of therapeutic copper into the hematopoietic centers in amounts that were too small to permit detection by chemical methods.

TABLE 1

Distribution of Copper Fed to Anemic Rats (*16*)

Percent of Copper Dosage 0.1 to 0.15 mg per rat

Type of deficiency—	*Copper*	*Iron*
Duration of therapy—	*24 hr*	*24 hr*
Number of rats—	9	4
	Percent	*Percent*
Blood	0.54	0.16
Liver	1.57	0.40
Kidneys	0.56	0.32
Spleen	0.14	0.02
Bone marrow	0.05	0.01
Carcass	2.54	1.43
Gastro-intestinal tract plus excreta	70.00	74.93
Retained	5.40	2.34
Recovered	75.40	77.27

In 1943, a group of German workers (*17*) reported the use of Cu^{64} for injection studies with dogs. The isotope was prepared by bombardment of metallic copper with deuterons. The irradiated target was dissolved in concentrated H_2SO_4 and used as copper sulfate. About four or five hours after irradiation, the radioactive copper sulfate in physiological salt solution was intravenously injected into two dogs. With one animal, the total activity after 15 hours was 870 μc in 39.5 mg of $CuSO_4$; with the other, it was 523 μc in 62 mg $CuSO_4$ after 25 hours. The samples were treated with H_2SO_4 and fuming HNO_3, and heated to complete oxidation. After neutralization with concentrated ammonia and the addition of about 10 mg of inert copper, the metal was precipitated in weak acid solution with sodium sulfide. The solution was filtered and, with samples of high activity, the measurements on the filter paper were made with an ionization chamber. The activities of weak preparations were measured with a Geiger-Müller counter.

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It was observed that the copper-64 was rapidly removed from the blood, indicating that the tissues picked up a considerable amount of the element from the first capillary passage. The copper in the red blood cells increased slowly; however, it remained at a high level for a longer period of time than in the plasma. The liver showed the largest copper accumulation of all the organs and also the greatest amount of copper per unit weight. Secretion of the copper in the bile occurred relatively slowly and it was suggested that the high copper of the intestinal contents were derived in part from secretion by the mucous membranes of the small and large intestine. It was interesting that of the radioactive copper in the kidney, most was found in the cortex. Relatively small amounts were found in the muscle tissue and even smaller amounts in the nerve tissues.

The use of pile-produced Cu^{64} in large- as well as small-animal studies has been reported by Comar, Davis and Singer (*18*). It was considered desirable to place emphasis on experimentation with the bovine in view of the apparent increased sensitivity of the ruminant species to copper deficiency.

The irradiation unit consisted of 0.32 gm of pure copper wire. As removed from the pile, it had about 100 mc activity. At the time of use the unit had decayed to about 20 mc. The copper was removed from the shipping container, immediately dissolved in a small volume of 8 *N* nitric acid, and was then neutralized with 2 *N* sodium hydroxide. A magnetic stirrer was used to provide vigorous agitation during neutralization to avoid precipitation of the hydroxide; the solution was adjusted as close as possible to neutrality without causing precipitation. Measured amounts were then removed for calibration standards and administration to the animals. Health precautions, handling of the samples, and procedures for radioactive assay have been discussed in detail in the first paper of this series.

From theoretical considerations, there would be anticipated no significant amounts of radiocontaminants in the unit, which would lead to the expectation that there would be no practical advantage gained by purification of the copper as received. The half-life of each sample was determined and found in good agreement with the established value of 12.8 hours. When the copper was purified by extraction from acid solution with dithizone, there was no observable change in the half-life. Perhaps of most significance were experiments in which the blood plasma was analyzed chemically for copper before and after administration of the radioactive preparation; the increase in plasma copper as determined chemically agreed fairly well with the values obtained by activity measurements. This means that so far as accumulation in the plasma was concerned the stable and radioactive atoms of copper behaved identically.

The actual dosages used depended upon the specific activity of the preparation, the accumulation expected in the tissues, and the anticipated duration of the experiment. With rats, about 1 to 8 mg copper were used, with rabbits from 7 to 25 mg, and with cattle from 100 to 250 mg of copper.

It was apparent from excretion studies with all species that the absorption of even soluble copper was quite low. About 75% of soluble copper fed to the bovine was excreted in the feces and about 3% in the urine during the five days after administration. On the other hand, when the copper was intravenously injected only 6% of the dose was excreted in a like period, about equally in the feces and urine. This apparent high retention of injected copper confirmed a field experiment with cattle, which demonstrated that

injected copper exhibited a much longer period of therapeutic efficiency than did orally administered copper.

Table 2 presents typical tissue distribution values of labeled copper administered to cattle. Considering the distribution of the ingested copper, it was evident that although the retention by the animal was low, the copper which was absorbed was generally distributed and reached the tissues involved in hematopoiesis. The tissues showing a high concentration were, in decreasing order, the liver, kidney, gastro-intestinal tract, adrenals, thymus, gall bladder and bile; those of medium concentration included the pancreas, red bone marrow, intestinal lymph, blood, spleen, heart, lung and reproductive organs; very low concentrations of copper were found in the white bone marrow, muscle, hide, bladder, ligament, cartilage, bone, eye and nerve tissue.

It was obvious that the liver, which showed the highest concentration, served as the chief storage organ. The kidney invariably had the next highest concentration and in the adult bovine the ratio of liver to kidney accumulation averaged about five; in tissue distribution studies with rats sacrificed after 17 to 65 hours, the concentration of labeled copper in the kidney was found to exceed that in the liver, which pointed to a species difference and confirmed the results of Schultze and Simmons (*16*). With rabbits the liver-kidney ratio of labeled copper ranged from 13 to 30. Chemical analysis has shown that the livers of very young animals are especially high in copper and that a calf is born with a copper concentration in the liver of 4 to 8 times that in the liver of the adult; the data in Table 2 confirmed this selectivity and indicated that it persisted at least through the first 1½ months of life. In comparing the values from the young and the adult animals it is better to use the percent of dose figures, since the concentrations are affected by the body weight. It is noted that except for the liver the percentages of dose found in the various tissues were in close agreement; this indicated that the liver of the calf actually exhibited a greater selective accumulation of the absorbed copper.

In general, injection tissue values were about 10 times the corresponding ingestion values, which again reflected the poor absorption of the orally administered copper. Proportional distribution of the injected copper was similar to that of the ingested copper.

Since it is recognized that the gastro-intestinal tract has an important hematopoietic function, particular attention has been paid to the accumulation of copper in the true stomach and intestinal mucosa. It may be noted from Table 2 that in all cases the mucosal was greater than the muscular concentration; negative values for the duodenum were due in part to the small sample available. The ratio of mucosal to muscular concentration averaged 2.7 for ingested and 2.8 for the injected copper. Where the copper was injected the accumulation in the mucosa probably occurred via the general circulation, since it has been shown that relatively small amounts of copper reached the intestinal contents during the 24 hours following injection. Particularly in the case of the true stomach would it seem unlikely that the mucosal accumulation of the injected copper could have come from the contents. It is considered, then, that the gastro-intestinal mucosa do concentrate copper from the general circulation, but an estimate of the extent of secretion into the lumen must await bile and pancreatic fistula studies.

Blood studies in cattle with Cu^{64} have led to the following picture in regard to the behavior of intravenously injected copper. Immediately after injection two processes occurred, removal of

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TABLE 2

Tissue Distribution of Labeled Copper Administered to Cattle

Mode of Administration	*Oral*		*Oral*		*Jugular Injection*	
Age and Weight of Animal	1½ *mo*, 85 *lb*		18 *mo*, 450 *lb*		18 *mo*, 460 *lb*	
Actual Dosage (mg Cu)	146		256		160	
Sacrificed After	42 *hr*		42 *hr*		19 *hr*	
Tissue	*γ per 100 gm fresh weight per 100 mg dosage†*	*Percent of dose in whole tissue*	*γ per 100 gm fresh weight per 100 mg dosage†*	*Percent of dose in whole tissue*	*γ per 100 gm fresh weight per 100 mg dosage†*	*Percent of dose in whole tissue*
Pituitary	*	0	*		35	0.00059
Thyroid	*	0	*		17	0.0046
Thymus	32	0.032	3	0.067	19	0.024
Adrenals	48	0.0015	3	0.00045	28	0.0033
Reproductive organs	5	0.0017	1	0.0058	8	0.056
Cerebrum	*	0	*		1	0.0020
Cerebellum	33	0.008	*		2	0.0016
Eye	*	0	*		6	0.0042
Intestinal Lymph Glands	13		3		29	
Heart	8	0.019	1	0.012	11	0.088
Blood	10	0.29	2	0.25	60	9.4
Aorta	*	0	3	0.0019	23	0.013
Lung	8	0.037	1	0.022	66	0.96
Trachea	7	0.0031	*		100	0.021
Kidney	71	0.10	9	0.045	15	0.72
Bladder	4	0.0013	1	0.007	20	0.014
Bladder urine	69	0.0066	17	0.040	29	0.010
Tongue	6	0.011	2	0.015	10	0.068
Esophagus	3	0.0012	2	0.0059	14	0.029
Omasum	100	0.075	3	0.046	13	0.16
Omasum contents	690	0.38	61	2.0	*	
Fundus abomasum, mucosa	42		6		27	

Omasum contents	690	0.38	61	2.0	*	
Fundus abomasum, mucosa	42	0.042	6	0.032	27	0.15
Fundus abomasum, muscular	13		3		10	
Pyloric abomasum, mucosa	44		11		33	
Pyloric abomasum, muscular	9		3		12	
Abomasum contents	100	0.12	39	0.57	2	0.023
Reticulum	17	0.011	4	0.025	28	0.15
Rumen	13	0.033	2	0.055	33	1.2
Rumen and reticulum contents	310	7.8	40	11.0	*	
Duodenum, mucosa	*	0.38	10	0.097	51	0.28
Duodenum, muscular	10		*		20	
Jejunum, mucosa	31		4		34	
Jejunum, muscular	16		3		15	
Ileum, mucosa	32		4		20	
Ileum, muscular	14				18	
Small intestine contents	50	0.21	70	2.2	6	0.15
Large intestine mucosa	45	0.10	8	0.12	61	1.8
Large intestine muscular	13		4		12	
Large intestine contents	310	0.67	750	29.1	18	0.6
Pancreas	17	0.0074	2	0.0024	87	0.21
Spleen	9	0.012	3	0.015	43	0.20
Liver	1090	7.0	41	1.0	1130	32.6
Gall bladder and bile	97	0.0056	2	0.0036	190	0.1
Tenderloin muscle	6		1			
Gastrocnemius muscle	*		*		4	
Ligament	*		1		11	
Cartilage	*		*		7	
Bone	*		*		*	
Red bone marrow (ribs)	15		2		51	
White bone marrow (long bones)	9		*		21	
Teeth	*				*	
Hide	5		1		9	

* No radioactivity detected in sample. † γ represents micrograms of Cu.

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the copper from the plasma by deposition in the tissues, and absorption of copper by the red blood cells. The first process occurred initially at a much faster rate than the second; after the large initial absorption of copper by the tissues, which took place within five minutes after injection, there was practically no removal of copper from the blood for about an hour, but the red blood cells continued to accumulate copper from the plasma. Between one and three hours there was further removal of copper from the blood with the indication that most, if not all, of the copper was being removed by the tissues from the plasma. From then on, attainment of equilibrium between the red blood cell and plasma copper proceeded at a faster rate than removal of copper from the blood.

The low copper content of milk has long been recognized. In order to study directly the secretion of dietary copper in the milk, 289 mg of labeled copper were fed to a dairy cow. Only 0.005% of the dosage was found in the milk (*19*).

The results to date with radioactive copper are in general agreement with such findings as are available in the literature and which were obtained by chemical analysis. Locational problems in the normal animal have been somewhat clarified, and it is anticipated that studies of deficiency conditions, interrelationships of various factors, and functional aspects will be the next logical approach.

The Molybdenum Problem

In 1938, Ferguson *et al.* (*20*) discovered that naturally occurring molybdenum in certain pastures in the United Kingdom was responsible for a severe disease of cattle and sheep. The unhealthy pastures were characterized by a molybdenum content of 20 to 100 ppm on the dry basis, as compared with less than 5 ppm in the normal pasture. The experimental production of the disease by administration of sodium molybdate to healthy cattle confirmed the toxic action of this element. Potentially toxic levels of molybdenum have since been reported in parts of Florida and California (*21*, *22*).

A most satisfactory feature of the molybdenum problem has been the finding that supplemental copper will adequately cure or prevent the condition. The symptoms of this disease are quite similar to those of copper deficiency, and the therapeutic action of copper indicates a relationship between these two elements which is as yet unclear. McGowan and Brian (*23*) have recently suggested the following theory: The activity of bacteria in the gastro-intestinal tract is controlled by catechols; molybdates reduce the effective concentration of catechols by formation of complexes and the uncontrolled bacterial activity becomes excessive and causes the condition which is manifested by extreme diarrhea; the therapeutic effect of copper is due to its toxic action on the bacteria. This theory is tempting, and would account for observations that ruminants are more susceptible to an inbalance of molybdenum and copper than are single-stomached species; however, further confirming support is required before it can be accepted unreservedly.

There has been no suggestion that molybdenum is beneficial for animals other than a claim (*24*) that a molybdenized iron sulfate gave more rapid hemoglobin formation than iron sulfate in patients with an iron deficiency anemia. Teresi *et al.* (*25*) stated that if molybdenum is required by the growing rats, this need is satisfied by 0.5 micrograms per day. Fairhall *et al.* (*26*), in a Public Health Bulletin, have presented a comprehensive compilation of the literature on molybdenum to 1945. This report also describes an experimental study of the toxicity of

molybdenum from the point of view of the industrial hazard. It was found that soluble molybdenum compounds such as molybdenum trioxide, calcium molybdate and ammonium molybdate when fed to rats and guinea pigs in large doses of from 1,200 to 6,000 mg per kg invariably proved fatal. The fatalities were much less at a 120 to 600 mg level. There were no fatalities when as much as 6,000 mg molybdenum as MoS_2 per kg of body weight were ingested. Intraperitoneal injection experiments indicated a high mortality rate for guinea pigs injected with soluble molybdenum compounds in amounts of from 400 to 800 mg per kg. Tissue analyses indicated that the greatest storage of molybdenum occurred in the kidneys and the bones. Both the absorption and excretion of this element were shown to be rapid.

The apparent interference in bone metabolism as a result of copper deficiency and/or molybdenum toxicity may be related to both the tendency of molybdenum to be stored in the bone and the observed inhibitory action of molybdates on phosphatase activity (*27*, *28*).

While from the animal nutrition standpoint molybdenum in the diet is considered as undesirable, it should be noted that this element is considered an essential for plant growth. Anderson (*29*) has reviewed the literature on the role of molybdenum in plant nutrition and has pointed out that in many areas in Australia this element must be applied for the establishment and satisfactory production of subterranean clover. It is to be emphasized that any fertilization program should take into account the health of the animals to be maintained on the molybdenum-treated pasture. There are many problems in plant nutrition such as the greater requirement and uptake of molybdenum by legumes, the effect of phosphorous on molybdenum utilization by the plant, and the effect of *p*H on the absorption of this element which could be advantageously studied by tracer methods.

Radioisotope Studies with Molybdenum: Mo^{99}, of half-life 67 hours, is the isotope used for tracer studies. It is available as a pile-produced irradiation unit containing initially about 40 mc of activity in 10 gm MoO_3. The methods of assay and preparation of the samples may be carried out as described in the first paper of this series. Molybdenum is better suited than copper for animal tracer studies because of its somewhat longer half-life, its relatively lower toxicity and its greater absorption by the animal.

Biological studies in this laboratory with Mo^{99} were performed as follows (*30*): Pile-produced Mo^{99} was obtained in 10 gm of MoO_3. The material as received was transferred to a 400-ml beaker and 35 ml of 14.3% NaOH was added. The mixture was stirred mechanically and a clear solution obtained in 1 to 12 hours. The solution was then made to a convenient volume with distilled water for use. The *p*H was near 7. No significant radiocontaminants would be expected in this unit on the basis of the analysis of the target material; the measured half-life agreed well with the established value of 67 hours.

When Mo^{99} was fed to a steer, about 34% of the dose appeared in the feces during 14 days and about 45% in the urine; this indicated the relative high absorption of soluble molybdenum. Following intravenous injection, about 11% of the dose appeared in the feces and 37% in the urine after six days. Complete tissue distributions have been determined similar to those reported in Table 2 for copper. Highest concentrations of labeled molybdenum were found in the bone, liver, teeth, intestinal lymph glands, intestinal mucosa, kidneys, spleen, eye and red bone marrow; low values were found for the brain and intermediate values for other tissues.

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TABLE 3

Accumulation of Ingested Mo^{99} in Blood and Liver of the Bovine (*30*) (Percent of Administered Dose)

Time (Hr)	*Blood*	*Liver*
16	0.60	0.26
41	2.9	0.51
64	2.6	0.42
95	1.5	....
114	....	0.35
138	0.70	....
186	0.19	....
306	0.07	....

Table 3 shows the accumulation of ingested Mo^{99} in the blood and liver of a heifer in percent of the administered dose. The total blood was calculated as 7.7% of the body weight; the liver samples were taken by biopsy and the total weight of the liver estimated from experience. The peak of accumulation was reached in both the blood and the liver at about 41 hours with the concentrations decreasing thereafter.

In view of the similarity in the metabolic behavior of molybdenum and phosphorous in the animal, an experiment was performed to determine the extent to which dietary molybdenum was secreted in the milk (*19*). About 7 gm of the Mo^{99} preparation was fed to a dairy cow and the milk collected for radioactive assay. About 2% of the dosage was found in the milk over a five-day period; this was somewhat lower than phosphorous secretion where about 10% is usually recovered, but much higher than copper secretion.

Nielands, Strong and Elvehjem (*31*) have recently reported on molybdenum in the nutrition of the rat. It was noted that with the growing rat, a level of 500 mg percent of molybdenum as sodium molybdate resulted in death after the first week, whereas levels of 100 and 50 mg percent permitted a greatly reduced growth rate; these rats showed no obvious gross pathology or change in the blood picture. The toxicity of a diet containing 40 mg percent of molybdenum was largely overcome by feeding an additional 2 mg percent of copper to a diet already containing 7.73 mg percent of copper. Whole liver substance protected against molybdenum, but iron, zinc or cobalt showed no such effect.

These workers also used pile-produced Mo^{99} in tissue distribution studies. The sample of radioactive molybdic acid was dissolved in a stoichiometric amount of concentrated sodium hydroxide and the neutral solution diluted to 50 ml of stock solution. The rat tissues were weighed in tared porcelain crucibles and ashed in a muffle furnace after caramelizing at 100° C. The ash was weighed; dissolved or suspended as evenly as possible in concentrated hydrochloric acid, and an aliquot transferred to a 50 mm lead dish and dried for Geiger counter assay.

The general tissue distribution was similar to that already described for molybdenum. The simultaneous administration of a dose of copper did not influence the distribution of the molybdenum. However, all tissues from two rats fed a simultaneous dose of catechol contained considerably more molybdenum after one day than the control group, which received only molybdenum. It would appear that the therapeutic effect of copper is not a simple formation of a less toxic, insoluble copper molybdate. There was insufficient data to allow evaluation of the role of catechol in this system.

The Zinc Problem

Although plant diseases due to zinc deficiency are widespread and of economic importance (*32*), no significant naturally occurring deficiencies of this element have been reported for animals. Nevertheless, zinc has been recognized

as a dietary essential for animals since 1922. Hart and Elvehjem (*33*) have reviewed the literature on zinc to 1936. A possible clue as to the function of this element came from the findings that zinc was chemically bound in the crystalline insulin molecule, and that the injection of zinc salts together with crystalline insulin produced a far less drastic hypoglycemia than insulin alone. Hove *et al.* (*34*), in 1937, observed that rats receiving 22 micrograms of zinc per day showed deficiency symptoms, whereas the deficiency was prevented by a level of 40 micrograms per day. These workers postulated that zinc was involved in the production or utilization of some hormone of the pituitary which controlled the motility and tonus of the intestinal tract.

In addition to insulin, zinc has been shown to form a part of the enzyme, carbonic anhydrase, and has also been found in purified preparations of uricase. It has been reported that a zinc deficiency decreases the activity of carbonic anhydrase and also the activity of intestinal phosphatase and blood phosphatase. A more recent review on zinc has been published in 1945 by Hegsted *et al.* (*35*). Day and Skidmore (*36*) recently reported that a zinc deficiency in mice markedly reduced the catalase activity of the liver and kidneys, but did not affect the blood catalase. Smith and Larson (*37*) observed that an anemia caused by feeding zinc salts to rats was counteracted by feeding additional copper salts. This is another example of interactions between elements, and points to the occurrence of relative deficiencies where animals may be deficient in one mineral relative to an excess of some other element.

Radioisotope Studies with Zinc: Zn^{65}, half-life 250 days, is the isotope most suitable for trace biological studies. Zn^{69}, half-life 38 minutes, has had limited use in therapeutic investigations where the short half-life was a very desirable feature. As with the other trace elements already discussed, in evaluation of the suitability of any given preparation, the specific activity, the sensitivity of the assay, the physiological dose for the experiment, and the accumulation in the tissues of interest must be taken into consideration.

Cohn *et al.* (*38*), in 1939, employed Zn^{65} in physicochemical studies of insulin. The measurements were made on dried crystals of the protein with a Lauritsen-type quartz-fiber electroscope. The radiation was filtered through 2.35 mm of aluminum so that only the gamma rays were recorded; this avoided uncertainties due to self-absorption of the beta particles in samples of varying bulk. Repeatedly electrodialyzed crystalline zinc insulin was crystallized with Zn^{65} from acetate buffers and no more than 0.31% of the radioactive zinc was detected in the final products of crystalline insulin. This was lower than the expected value of 0.52%, which has been reported for the zinc content of crystalline zinc insulin. The experiments indicated that none of the Zn^{65} introduced into insulin was removed at neutral reactions by electrodialysis or prolonged dialysis, but that at the isoelectric point of insulin the radioactive zinc was quantitatively lost to normal horse serum. When, however, insulin containing two atoms of radioactive zinc per mole was separated from serum at neutral reaction, by precipitation with the protamine, salmin, the resulting precipitate retained 0.14% radioactive zinc, corresponding approximately to a mono-radioactive zinc insulin protaminate.

In 1943, Sheline *et al.* (*39*) reported on the excretion of intravenously injected Zn^{65} into the urine and feces of the dog and mouse. The radioactive zinc was obtained by washing the copper deflector plate of the cyclotron with cotton moistened with concen-

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trated nitric acid. The resultant solution was freed of nitric acid by repeated evaporations with HCl. The copper was removed by repeated precipitations with H_2S in 0.5 *N* HCl. The filtrate was evaporated to dryness to remove the H_2S, the residue taken up in 0.5 *N* HCl and transferred to a separatory funnel, 0.5 ml of 20% citric acid added, the solution made alkaline with NH_4OH, and the zinc removed by extraction with a chloroform solution of dithizone. The chloroform phase was washed with dilute ammonia water to remove excess dithizone and the zinc extracted from the chloroform layer with 0.1 *N* HCl. The zinc was finally used as a solution of its chloride. In order to test the preparation for possible radiocontamination with Co, Ni, Pb and Cd, small quantities of these elements were individually added to aliquots of the zinc solution. Each element was then separated chemically from the zinc and the separated element tested for radioactivity. Since no activity was found, it was concluded that the original solution was free of the radioisotopes of Co, Ni, Pb and Cd.

In the case of the mice, the feces and the urine collected on filter paper were ashed at 450° C. The ash was transferred to squares of blotter paper, which were then wrapped in cellophane, and its radioactivity determined with a Geiger-Müller counter. No self-absorption effects were observed due to varying amounts of ash. In the analyses of dog excreta, the samples of urine and feces were dried and ashed at 450° C for 12 to 18 hours. If at this time appreciable amounts of unashed material remained, the soluble portion was dissolved in HCl and filtered off, the unashed fraction returned to the muffle, and the ashing continued. The HCl solution was filtered into a volumetric flask and diluted to volume. Suitable aliquots were pipetted into beakers and diluted to 25 to 30 ml, approximately 30 mg of zinc as the chloride were added, and the solution was nearly neutralized with dilute NaOH. The zinc was precipitated as the carbonate by the addition of a saturated solution of K_2CO_3 with care being taken not to add a large excess of the latter. After coagulation, the precipitate was filtered through a 5.5-cm filter paper. The paper was removed from the funnel and the edges trimmed to form a rectangle. The precipitate was spread over the surface of the filter paper and dried with an electric light bulb. The sample was then wrapped with two-inch Scotch tape and was ready for radioactive assay.

Each mouse received an intravenous dosage of 0.33 micrograms labeled zinc, and the dogs, which weighed about 4.5 kilos, received about 6 micrograms. In the mouse, as much as 50% of the zinc dosage was eliminated in the feces during 170 hours, while in the dog about 25% was found in the feces at the end of 12 to 14 days. In like periods, a total of 2% of the dosage was found in the urine of the mouse, and 1.2 to 4.7% of the dosage in the urine of the dog. This indicated that a large fraction of body zinc was eliminated by way of the gastro-intestinal tract.

This investigation was later extended by the same workers to include a detailed study of the tissue distribution of labeled zinc administered to mice and dogs (*40*). The general techniques were as described above. The radioactivities in the whole blood, plasma, and corpuscles were determined by pipetting one ml of each fraction into rectangular dishes, 2×6 cm, made from aluminum foil that had been lined with lens paper. In the case of some of the small mice tissues, the samples were weighed and uniformly spread over a rectangular piece of blotting paper, 2×6 cm, and wrapped in cellophane. They were allowed to dry before their radioactivity was determined.

Five dogs were injected intravenously with 6.5 to 16.3 micrograms of labeled zinc as the chloride, and sacrificed after 3, 8, 24, 94 and 170 hours. A total of 39 mice received intravenous injections of 0.33 to 1.6 micrograms, and groups of 3 to 7 animals were sacrificed after ¾, 2, 8, 26, 72 and 170 hours. The injected zinc disappeared rapidly from the plasma; none was detected in the plasma of the dog 10 hours after its injection into the blood stream. The labeled zinc appeared early in the red blood cells and continued to increase therein during the entire period of observations. At the early intervals, maximum deposition occurred in the liver; after three hours the dog's liver contained 38% of the dosage, while that of the mouse contained 25% at the two-hour interval. The most active uptake of Zn^{65} (uptake and loss) was observed in the liver, pancreas, kidney and pituitary gland. The least activity was found in the red blood cells, brain, skeletal muscle, and skin; the activities of the spleen, gastro-intestinal tract, adrenals, lungs, lymph nodes, bone, heart, and thymus were intermediate. Such tissues as the blood corpuscles, bone, nervous system, skin and skeletal muscle were characterized by either a slow deposition increasing with time or by maintenance of the small amounts deposited at the early intervals.

Experimental findings have suggested that the pancreas may be concerned with the metabolism of zinc in the animal. On this basis, Montgomery, Sheline and Chaikoff (*41*) employed Zn^{65} to study its elimination in the pancreatic juice, duodenal juice, and bile of the dog. The procedures for preparations of tissues and radioactive assay were essentially as described above. One dog was prepared with a pancreatic fistula, two with pancreatic and biliary fistulas, one with biliary and duodenal fistulas, and one with biliary, duodenal and pancreatic fistulas. The labeled zinc chloride was injected intravenously into a hind leg vein.

Considerable amounts of the labeled zinc were found in the intestinal juice obtained from the duodenum. A large proportion of the dosage was eliminated by way of the external secretion of the pancreas; as much as 11% was excreted in the pancreatic juice in 14 days. The high concentration of Zn^{65} in the pancreatic juice as compared with the exceedingly low concentrations of the isotope in the plasma, indicated that the acinar cell was able to concentrate zinc. In contrast to the pancreatic secretion, very little zinc was eliminated by way of the bile. The maximum excretion observed for this pathway was 0.4% in 8 days. This was interesting in view of the high initial liver accumulations and indicated that considerable amounts of the element originally deposited in the liver were removed for uptake by other tissues.

An investigation of zinc metabolism based on the use of Zn^{65} is currently in progress at the Harvard Medical School. The only published information available is an abstract by Vallee and Fluharty (*42*). Samples of blood, white cells, and tissue were dry-ashed and the zinc extracted with dithizone for photometric determination. The zinc was removed from the dithizonate with sulfuric acid and electroplated from an alkaline solution with added carrier zinc on a copper disk. The counting procedure was similar to that used for Fe^{55} (*43*). The complete separation of white blood cells from blood was accomplished by flotation of heparinized whole blood on an isosmotic solution of bovine serum albumin of specific gravity approximately 1.079.

It was observed, upon external scanning with a Geiger-Müller counter, that intravenously injected zinc became widely distributed throughout the entire body of the normal dog. Simultaneous measurements of Zn^{65} and total

zinc yielded information on the normal zinc content of the following organs, and also indicated that there was no selective accumulation of the element in these organs: heart and great vessels, respiratory organs, digestive organs, genito-urinary tract, muscle, cortical bone, brain, endocrines, lymph glands, liver, spleen, marrow, plasma and whole blood. Following intravenous injection, it was found that the Zn^{65} became concentrated within the circulating white cells in amounts sufficient for radioactive assay in the leukocyte mass separated from 15 cc of whole blood.

Iron and iodine are also classed as nutritional trace elements; however, radioisotope studies with these two elements are already extensive, in distinction to those discussed here, and would warrant individual review articles. In considering the literature on the radioisotopes of cobalt, manganese, copper, molybdenum and zinc, one is impressed with the scarcity of published material. It is anticipated that widespread utilization of these techniques will result from the increased availability of isotopes, trained personnel, and adequate instrumentation.

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ANALYSIS OF SCALE UNITS

Ideal operating conditions of scale circuits are analyzed theoretically, the transfer from one equilibrium condition to the other being broken into two transient conditions. Influence of equilibrium states and intrinsic time constant on resolution and stability is studied; practical design considerations for advanced scales and types of scalers are discussed

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SCALE-OF-N CIRCUITS are important tools for counting radiations in nuclear physics, as well as for various other applications. Radiation counters deliver electrical impulses theoretically distributed randomly with time. The basic function of scale-of-N circuits is to give one output pulse, which can be registered by an electromechanical indicator, for every N pulses fed into the circuit. Various types of scaling units have been described, however this discussion is limited to the most common type, the scale-of-2 circuit that is derived from the Eccles-Jordan trigger circuit. The operating conditions and design of these circuits will be analyzed theoretically, taking into consideration the transient and equilibrium conditions and the switching problem, and thus laying a basis for designing scalers with high resolution.

For nuclear research two principal characteristics need to be considered: (1) stability of the electronic counting and (2) resolving power of the entire scaling apparatus. The trend in this field is to greater resolution without impairing the stability commonly obtained with slower circuits. In general the scaler consists of scale-of-2 units arranged to provide an over-all scale-of-N circuit. The basic scale-of-2 unit has two distinct and reversible equilibrium conditions that are commutable by suitable triggering or switching waveforms. The switching initiates transients leading to the inverse equilibrium. Hence three phenomena have to be considered: (1) the equilibrium, (2) the transient and (3) the triggering. These will be analyzed in logical sequence.

Equilibrium Condition

A particular form of the scale-of-2 unit is shown in Fig. 1. In the common case resistor R_4 is zero, but is here taken into account. The two tubes, designated A and B, are alternately conducting or cut off. If tube B has an anode current i_T, tube A is cut off and has an anode current i_0, which, if existent, is vanishingly small. These conditions correspond to one condition of equilibrium; for the other, tube A is conducting and tube B is cut off.

Assuming a symmetrical circuit, we can express the equilibrium conditions by the following relations

$$E_a + E_b = E_0 = R_1 i_1' + R_2 i_1 + R_2 i_2' + R_4(i_2 + i_2') \quad (1)$$

$$E_a + E_k = E_0 = R_1 i + R_2 i_2 + R_3 i_2 + R_4(i_2 + i_2') \quad (2)$$

$$i_1' = i_2' + i_g + i_0 \quad (3a)$$

$$i_1 = i_2' + i_g \quad (3b)$$

$$i = i_2 + i_T \quad (3c)$$

The branches in which these currents flow are indicated in Fig. 1; E_k is the bias, E_a the anode supply voltage, and i_g is the grid current drawn by the conducting tube.

Solving for i_2, we obtain

$$i_2 = [(R_1 + R_2 + R_3)i_2' + R_2 i_g - (i_T - i_0 - i_g)R_1]/[R_1 + R_2 + R_3] \quad (4)$$

which can be written

$$i_2 = i_2' - i_E \quad (5)$$

where i_E is defined by

$$i_E = \frac{R_1(i_T - i_0 - i_g) - R_2 i_g}{R_1 + R_2 + R_3} \quad (6)$$

Let E_1 be the potential difference across R_4, then

$$E_1 = R_4(i_2 + i_2') = R_4(2i_2' - i_E) \quad (7)$$

and the grid potential e_g on the conducting tube can be written

$$(e_g)_B = E_1 + R_3 i_2' \quad (8)$$

where

$$i_2' = \frac{E_0 - (R_1 + R_2)i_g + R_4 i_E - R_1 i_0}{R_1 + R_2 + R_3 + 2R_4} \quad (9)$$

In order to obtain an effective bias voltage E_g on tube B with

$$(e_g)_B = E_k - E_g \quad (10)$$

a bias supply E_k should be applied that satisfies the expression

$$E_k = \frac{E_a(R_3 + 2R_4) + E_g(R_1 + R_2 + R_3 + 2R_4)}{R_1 + R_2} - R_4 i_E - (R_3 + 2R_4)i_g - \frac{R_1(R_3 + 2R_4)}{R_1 + R_2} i_0 \quad (11)$$

The other tube potentials for the equilibrium under consideration are

$$(e_g)_A = E_1 + R_3 i_2 \quad (12a)$$

$$(e_a)_B = E_0 - R_1 i \quad (12b)$$

$$(e_a)_A = E_0 - R_1 i_1' \quad (12c)$$

For the second equilibrium condition

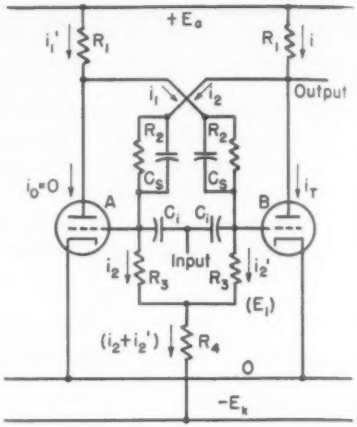

FIG. 1. General circuit under discussion

(tube B cut off), we only have to commute the subscripts A and B in the foregoing relations.

Both equilibrium conditions are not simultaneously possible as a stable condition. Their difference can be expressed by the voltage changes occurring in the anode and control grid potentials as follows. By definition, let ΔE_a and ΔE_g be given by

$$\Delta E_a = (e_a)_A - (e_a)_B = R_1(i_T - i_g - i_0 - i_E) = R_1(i_T^* - i_E) \quad (13)$$

$$\Delta E_g = (e_g)_B - (e_g)_A = R_3 i_E \quad (14)$$

from which the importance of the current i_E is evident, and, denoting by ΔE the grid potential swing from zero to the cutoff voltage, called also the grid base, under the effective operating conditions, the equilibrium conditions can be characterized by the two following ratios

$$\frac{\Delta E_a}{\Delta E_g} = \frac{R_1}{R_3}\left(\frac{i_T^*}{i_E} - 1\right) \quad (15a)$$

$$\frac{\Delta E_g}{\Delta E} = \frac{R_3 i_E}{\Delta E} \quad (15b)$$

The foregoing shows that a scale unit can be built with various combinations

of numerical values for the components, even after a tube type has been chosen.

As the stability and resolution time depend largely on the components and tube parameters, which define the behavior of the scale unit, we will next devote our attention to the influence of these elements on the operating cycle of the unit.

Two Transient Conditions

The scale-of-2 circuit of Fig. 1 can be considered as a multivibrator, but with both halves overbiased so that operation with single, nonself-recurrent transients is possible. Thus the only steady state conditions are those of the two direct-current equilibriums. To trigger the circuit, switching signals must be applied to the grids or the anodes. Usually these signals are delivered as pulses from the input circuit or as potential jumps from another scale unit. The switching pulse then initiates an internal transient that produces the change from one equilibrium condition to the other.

As previously mentioned, one of the fundamental properties of a scaler is its resolving power. Resolution time can be defined as the time interval between the start of a triggering waveform, which produces the transient change of equilibrium, and the arrival at the new equilibrium condition, or at least to the condition at which the new equilibrium is sufficiently established so that it can be identified by the associated equipment and at which the sensitivity of the circuit has been restored so that it can be retriggered.

Corresponding to the two equilibrium conditions of a symmetrical unit are two transient conditions, which we will call transient I and transient II, respectively, for decreasing and increasing anode potentials of the tube being switched. Both these transients occur simultaneously during a transfer of equilibrium and result from the switching action and the internal transients.

Even for the self-regenerating oscillation cycle of a common multivibrator with only capacitive internal couplings, rigorous calculation of the waveforms is impossible. Hence, in the case of the scale-of-2 unit, where a given transient state may depend on previous transients, which may be irregularly spaced especially when the resolution time limit is approached, rigorous calculation of the transient waveforms is unfeasible. However, the triggered character of the operation enables us to consider only one transfer occurring after a long rest period.

Assuming an instantaneous switching off of the conducting tube, and the remaining of this tube cut off for awhile, the loop gain of the remaining active portion of the circuit with feedback is zero and there can be no regenerative instability. If, on the other hand, the grid switching is not instantaneous, it is accelerated at the beginning of the transfer by an instability cycle. In either case the fastest possible anode transient is that of the ideal case, and its time constant can be called the intrinsic time constant of the unit.

Because one of the grids is below and the other above cutoff, a scale unit could be triggered by a positive or a negative voltage step. Triggering by a negative step is, however, preferred because it is easier to realize units which are insensitive to positive pulses, and hence can discriminate between triggering pulses and spurious (positive) ones. Negative pulse fronts are generally steeper (pulse rise is independent of grid current flow), permitting more ideal switching and amplitude discrimination with a differentiating type of coupling between scale units.

The equivalent circuit of a scale unit can be divided into two identical and independent halves so far as transient behavior is concerned. One such half

is represented by Fig. 2. During switching, the working point on the tube's characteristic moves from one to the other of two fixed points, corresponding to the two equilibriums. The dynamic plate resistance r_p can be taken from the i_p, v_p characteristic. For pentodes operating below the knee of their characteristic and for triodes, the dynamic r_p for $v_g = 0$ (or slightly positive) is practically equal to the static tube resistance ρ for such a working point. The tube can thus be represented by a branch containing a resistance ρ in series with a switch, in the case of instantaneous switching.

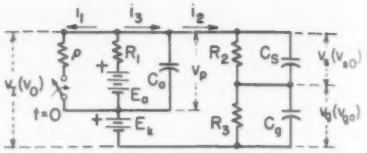

FIG. 2. Equivalent circuit of one independent half of the scale unit during transient condition I

Transient Condition I

In the case of decreasing anode voltage, the tube branch is closed at zero time. The following notations will be used in the analysis

v_g: instantaneous grid voltage, the initial value of which is v_{g0}

v_a: instantaneous anode voltage, the initial value of which is v_{a0}

v_s: instantaneous voltage across C_s, initial value v_{s0}

C_s: cross-coupling capacitance shunting R_2

C_g: total capacitance affecting the tube grid of the coupled tube, including interelectrode, wiring and input coupling circuit capacitances, and the Miller effect capacitance (calculable from the actual simultaneous voltage variations on the grid and other electrodes of the coupled tube, which does not act as a linear amplifier)

C_a: total capacitance affecting tube anode

The transient analysis will be performed using the Laplace transformation, taking into account the initial voltages. The transform equations for the circuit of Fig. 2 are

$$i_2 = v_s/R_2 + pC_s(v_s - v_{s0}) = v_g/R_2 + pC_g(v_g - v_{g0}) \tag{16}$$

$$i_2 = i_3 + pC_a(v_p - v_{p0}) = i_3 + pC_a(v - v_0) \tag{17}$$

$$E_a + E_k = E_0 = R_1(i_1 + i_2) + v \tag{18}$$

$$v = E_k + \rho i_1 = v_g + v_s \tag{19}$$

From Eq. 16 it follows that

$$v_g = \frac{p(\tau_g v_{g0} - \tau_s v_{s0})}{1 + p\tau_g} + \frac{R_2\,1 + p\tau_s}{R_2\,1 + p\tau_g} v_s \tag{20}$$

Eliminating v_g and v_s leads to the transform equation for v

$$v(p) = \frac{a_2p^2 + a_1p + a_0}{b_2p^2 + b_1p + b_0} \tag{21}$$

where the coefficients are defined as

$a_0 = E(R_2 + R_3)$

$a_1 = E(R_3\tau_s + R_2\tau_g) + \tau_a v_0(R_2 + R_3) + \tau v_{s0}(R_2 + R_3) + mR_2(\tau_g v_{g0} - \tau_q v_{s0})$

$a_2 = v_0(\tau_a\tau_s R_3 + \tau_a\tau_g R_2 + \tau\tau_g R_2) + \tau\tau_s R_3 v_{s0} - \tau\tau_q R_2 v_{s0}$

$b_0 = g(R_2 + R_3) + mR_2$

$b_1 = q\tau_s R_3 + \tau_g R_2(m + g) + \tau_a(R_2 + R_3) + \tau R_2$

$b_2 = \tau_g\tau_s R_1 + \tau_a\tau_s R_3 + \tau\tau_g R_2$

$$E = E_0 + fE_k$$
$$R_1 = f\rho; \qquad mR_2 = R_1; \qquad nR_2 = R_3$$
$$g = f + 1; \qquad q = n + 1$$
$$\tau = C_s R_1; \qquad \tau_g = C_g R_3; \qquad \tau_a = C_a R_1; \qquad \tau_s = C_s R_2; \qquad \tau_q = C_s R_3$$

In order to obtain the inverse transform $v(t)$, the nature of the roots of the characteristic equation

$$b_2 p^2 + b_1 p + b_0 = 0 \tag{22}$$

taken from the denominator of Eq. (21) has to be investigated. For a passive circuit containing only R and C, the condition for overdamping is always fulfilled; that is, the conditions for the two real and negative roots are satisfied, which are

$$(b_1/2b_2)^2 - (b_0/b_2)^2 > 0 \tag{23a}$$
$$(b_1/b_2) > 0 \tag{23b}$$

Denoting the roots by $-\chi_1$ and $-\chi_2$, the time function $v(t)$ corresponding to $v(p)$ can be written

$$v_1(t) = \frac{1}{b_2}\left\{\frac{a_0 b_2}{b_0} + \frac{1}{\chi_1 - \chi_2}\left(\chi_1 a_2 - a_1 + \frac{a_0}{\chi_1}\right)\epsilon^{-\chi_1 t} - \frac{1}{\chi_1 - \chi_2}\left(\chi_2 a_2 - a_1 + \frac{a_0}{\chi_2}\right)\epsilon^{-\chi_2 t}\right\} \tag{24}$$

Verifying for $t = 0$ and $t = \infty$, we find the values

$$v(0) = v_0$$
$$v(\infty) = \frac{(E_a/R_1) + E_k(R_1 + \rho)/R\rho}{(R + \rho)/R\rho + 1/(R_2 + R_3)}$$

Once $v(t)$ is known, v_g can be obtained as a function of $v(t)$ by the following operational form

$$v_g = \frac{1}{C_t}\left\{C_s \frac{p}{p + \beta} v(t) + \frac{1}{R_2}\frac{1}{p + \beta} v(t) + \frac{1}{R_3}(\tau_g v_{g0} - \tau_q v_{s0})\frac{p}{p + \beta}\right\} \tag{25}$$

where

$$\beta = \frac{R_2 + R_3}{R_2 R_3}\frac{1}{C_g + C_s} \tag{26}$$

from which the time function $v_g(t)$ is derived by application of a theorem of Duhamel

$$v_{g1}(t) = N\frac{1 - \chi_1\tau_s}{R_2 C_t(\beta - \chi_1)}(\epsilon^{-\chi_1 t} - \epsilon^{-\beta t}) - P\frac{1 - \chi_2\tau_s}{R_2 C_t(\beta - \chi_2)}(\epsilon^{-\chi_2 t} - \epsilon^{-\beta t}) + \left(\frac{\tau_g v_{g0} - \tau_q v_{s0}}{R_2 C_t} - \frac{M}{R_2 C_t \beta} + v_0\frac{C_s}{C_t}\right)\epsilon^{-\beta t} + \frac{M}{R_2 C_t \beta} \tag{27}$$

where $C_t = C_s + C_g$, and the coefficients N, P and M are from Eq. 24 written in the form

$$v_1(t) = M + N\epsilon^{-\chi_1 t} - P\epsilon^{-\chi_2 t} \tag{28}$$

The initial and end values of $v_g(t)$ are found for $t = 0$ and $t = \infty$ as

$$v_g(0) = v_{g0}$$
$$v_g(\infty) = MR_3/(R_2 + R_3)$$

Transient Condition II

When the anode voltage of one of the tubes rises, the grid voltage of the other tube is driven positive and soon grid current flows due to the coupling of C_s. To take care of this fact, a grid resistance can be introduced in shunt across R_3,

switched into the circuit when v_g reaches a given positive value.

If it is desired to calculate the delay time taken by the grid to reach cutoff, starting from the negative equilibrium value, then the subtransient conditions, during which the grid resistance ρ_g does not exist, have to be considered. In making the evaluation, the presence of a triggering pulse can be allowed for. Obviously ρ_g is not constant, but as far as its shunting effect on R_3 is concerned, a mean value can be taken.

Splitting the transient condition II into an interval of subtransient and one of transient II proper, we have the first case corresponding to Fig. 3 where the switch is opened at zero time. The circuit equations are Eq. 16, 17 and 29 with

$$E_a + E_k = E_0 = R_1 i_2 + v \tag{29}$$

Introducing the notations v_0', v_{g0}' and v_{s0}', instead of v_0, v_{g0} and v_{s0}, corresponding to the new initial values, we obtain for $v(p)$ an expression with the same form as Eq. 21:

$$v_{II}(p) = \frac{C_2 p^2 + C_1 p + C_0}{d_2 p^2 + d_1 p + d_0} \tag{30}$$

where

$$C_0 = E_0 R_1 (R_2 + R_3)/R_2 R_3$$
$$C_1 = v_0' C_a R_1^2 (R_2 + R_3)/R_2 R_3 + R_1 E_0 C_t + R_1^2 (R_2 C_a v_{s0} + R_3 C_g' v_{g0})/R_2 R_3$$
$$C_2 = v_0' R_1^2 (C_g' C_s + C_a C_g' + C_a C_s)$$
$$d_0 = R_1 (R_1 + R_2 + R_3)/R_2 R_3$$
$$d_1 = R_1^2 (R_3 C_g' + R_2 C_a)/R_2 R_3 + R_1 C_t + C_a R_1^2 (R_2 + R_3)/R_2 R_3$$
$$d_2 = R_1^2 (C_g' C_s + C_a C_g' + C_a C_s)$$

C_g' is the grid capacitance as produced by the Miller effect

For the roots of the new characteristic equation, the same remarks apply as for the foregoing case. Denoting the roots of the characteristic equation by $-\chi_3$ and $-\chi_4$, one finds for the time function $v(t)$

$$v_{II_s}(t) = \frac{1}{d_2}\left\{\frac{C_0 d_2}{d_0} + \frac{1}{\chi_3 - \chi_4}(\chi_3 C_2 - C_1 + C_0/\chi_3)\epsilon^{-\chi_3 t} - \frac{1}{\chi_3 - \chi_4}(\chi_4 C_2 - C_1 + C_0/\chi_4)\epsilon^{-\chi_4 t}\right\} \tag{31}$$

or

$$v_{II_s}(t) = M_1 + N_1 \epsilon^{-\chi_3 t} - P_1 \epsilon^{-\chi_4 t} \tag{32}$$

from which it also follows that the time function $v_g(t)$ has a form analogous to Eq. 27, where M, N and P, χ_1 and χ_2 are to be replaced by the new corresponding values.

At the end of the subtransient state a sudden network change occurs, caused by the shunting of R_3 by an additional resistance ρ_g, producing a branch resistance $r = \rho_g R_3/(\rho_g + R_3)$. This change in resistance could be replaced by an emf in series with R_3 and the resulting potentials could be found by the superposition theorem for linear networks. In order to find the values for the second transient condition II, r can be assumed to exist from zero time, and the equations for the subtransient state can be applied by changing R_3 into r. Denoting this change by an asterisk (*), we find finally for the expressions of the time functions $v(t)$ and $v_g(t)$

$$v_{II}(t) = M_1^* + N_1^* \epsilon^{-\chi_3 t} - P_1^* \epsilon^{-\chi_4 t} \tag{33}$$

and $$v_{gII}(t) = N_1^* \frac{1 - \chi_5\tau_s}{R_2C_t'(\beta^* - \chi_5)} \{\epsilon^{-\chi_5 t} - \epsilon^{-\beta^* t}\} - P_1^* \frac{1 - \chi_6\tau_s}{R_2C_t'(\beta^* - \chi_6)} \times$$

$$\{\epsilon^{-\chi_6 t} - \epsilon^{-\beta^* t}\} + \left\{\frac{\tau_g^* v_{g0}' - \tau_q^* v_{s0}}{rC_t'} - \frac{M_1^*}{R_2C_t'\beta^*} + v_0' \frac{C_s}{C_t'}\right\} \epsilon^{-\beta^* t} + \frac{M_1^*}{R_2C_t\beta^*} \quad (34)$$

where

$$\beta^* = \frac{r + R_2}{rR_2} \frac{1}{C_t'} \approx \frac{1}{rC_t'}$$

$$C_t' = C_g' + C_s \quad (35)$$

The ideal transient conditions are also defined as precisely as can be done in the face of the mathematical complexities. The intrinsic time constant of the unit can be calculated, as well as the waveforms. For design purposes the numerical calculations can be performed with many simplifications in the various terms according to the desired approximation.

The Transfer Action

As discussed in connection with the foregoing analysis, application of a negative wavefront to the grid of the conducting tube starts a transient voltage change on the anode of this tube. If the tube is cut off by a negative voltage step on the grid, the anode voltage rise is determined by the intrinsic time constant of the transient condition II. If the pulse front has a finite rise time, the corresponding anode potential rise can evidently not be faster than in the ideal case; the anode potential rise is then limited by the grid voltage change times the effective stage gain of that half of the unit.

The grid potential of the initially nonconducting tube reaches the space charge region with a finite rate of change, but is limited in its positive swing by grid current, which retards the rise of the coupled anode potential during transient condition II. The initially nonconducting tube is thus switched in with a finite switching time and the ideal transient on its anode for condition I is not reached. Instead, the decrease in anode voltage is determined by the rate of change of grid voltage on the tube. Increasing $\Delta E_g/\Delta E$ and $\Delta E_a/\Delta E_g$ permits approaching more closely to the ideal case. After a transmission delay, the grid of the initially conducting tube receives a supplementary negative pulse that can either increase the switching speed or increase only the negative swing of the grid. When the feedback signal reaches the grid before the tube is cut off, the instantaneous loop gain of the circuit may surpass unity, leading to a brief regenerative instability that may increase the switching speed so that the operation of the unit approaches more nearly to the ideal.

The particular form of the triggering wave may provide disturbing effects on the switching. If a rectangular pulse is applied, the back of the pulse can retrigger the unit if the pulse is wide enough (so that the circuit is ready for the action), or it may disturb the triggering, especially if the pulse is too narrow. Steep waveforms or very short triggering pulses on the grid approach the ideal case of instantaneous switching.

After this first part of the transfer, the grid potentials have passed their equilibrium values, and recovery to the equilibrium values follows at a rate determined by the slowest intrinsic time constants of the unit. The tube capacitances and the capacitive coupling from grid to grid inhibit the transfer but are neutralized by the grid-anode coupling capacitances, C_s, which assure the reliability of the transfer.

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Although the time constant R_2C_s is not an intrinsic time constant, it should be chosen large compared to the duration of the trigger waveform but small compared to the resolving time. The transfer initiated by a triggering action thus consists of a proper transference and a recovery. The transfer is intimately connected with the switching process, the transmission delay and the instantaneous loop gain.

Triggering the Unit

Reliability of a scaling unit depends largely upon the triggering. The coupling circuit between units and the shape of the triggering pulse have to be considered together. The triggering signals are designed in general as pulses, in which case precautions have to be taken to shorten as much as possible the rise time of the pulse front. To get the fastest switching, only direct pulse transmission to the grids (or plates), either by way of an adjustable capacitance or a diode, can be used. With capacitive coupling the signal appearing at the grid (in the absence of the transfer action) consists of a pulse even when a step voltage is applied at the input. Furthermore, capacitive coupling is simple, adjustable and provides (as note above) additional differentiating effect, but it increases the C_s of the preceding unit and the C_g of the following unit. Minimum C_i values should be used to reduce coupling between grids of a unit. Small series resistors have been used to decrease the capacitive loading on the preceding unit.

Diode coupling has the great advantage of providing unilateral coupling, but it is not direct, not easily adjusted and leads to more severe grid current limitation, diminishing the effective $\Delta E_s/\Delta E_g$ for rising anode potentials. Diode coupling prevents the disturbing effects of positive pulses. With capacitive coupling the disturbing

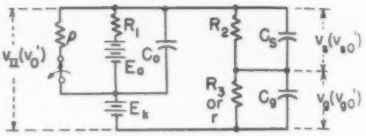

FIG. 3. Equivalent circuit during transient condition II; the switch simulates the behavior of the grid

effects of positive pulses and of excessive pulse widths must be reduced by grid current limitation and anode current saturation (by the effect of load R_1). Thus recovery to the equilibrium conditions is generally affected.

The case of finite switching times and nonlinear tube effects are not considered here.

Stability of a Scaler

Stability of a scale-of-2 circuit may be defined as the probability of obtaining a correct scaling action for a given interval, long enough, and for determined operating conditions, once the unit has been adjusted, in spite of instabilities and variations occurring in supply voltages, tubes, components and characteristics of the triggering pulse. Once reliable scaling action has been secured, there must be sufficient stability to keep the circuit from malfunctioning, which would be due to excessive asymmetry of the circuit, variations of capacitances or defective switching from insufficiently uniform triggering pulses, provided the mean pulse rate is not too high.

The final adjustment of a scaling unit for equilibrium conditions is generally done by manipulating the bias.

Figure 4 shows a stability diagram of a scaling unit that was obtained as follows: The currents i_g and i_T versus E_g, the tube being loaded by R_1, are known from the mean tube characteristic, or better, from measurement. Once these current curves are plotted, the values of ΔE_g and ΔE_s versus E_g

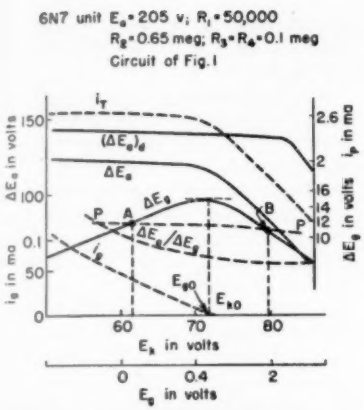

FIG. 4. From this type of plot, the range of possible stable operation of a scale unit can be determined

can be traced, as well as versus E_k, using Eqs. 15 and 13, respectively.

The ΔE_g versus E_k curve is the most important; it shows a maximum. To illustrate the existence of an adjustment range for the bias supply voltage, we draw a curve *PP* corresponding to the minimum ΔE_g that is needed to obtain correct scaling action for a given amplitude and shape of trigger pulse. By careful design, it is necessary to consider only the pulse amplitude because the pulse shape cannot vary much except for the first unit following an input.

The curve *PP* intersects the ΔE_g curve in two points, noted *A* and *B*, the abscissas of which delimit the ideal interval of E_k (or E_g) values satisfying

$$\Delta E_g > (\Delta E_g)_{\min} \qquad (36)$$

The wider this setting range for E_k, the better the stability that can be secured.

The curve *PP* can be found by assuming that $(\Delta E_g)_{\min}$ depends only on the amplitude ratio of the incoming pulses to the effective grid bias. If $e(+)$ and $e(-)$ designate, respectively, the peak amplitudes of the positive and negative pulses arriving at the control grid, there are two cases with which we must deal: (1) there are positive as well as negative triggering pulses so that

$$(\Delta E_g)_{\min} = |\Delta E| + |e(+)| \qquad (37)$$

and (2) there are only negative pulses (by some circuit arrangement) so that

$$(\Delta E_g)_{\min} = |\Delta E| \qquad (38)$$

The effective bias on the conducting tube E_{g0} corresponding to the minimum in the ΔE_g curve satisfies the expression $\Delta E - E_{g0} < |e(-)|$. Denoting the minimum value of the ratio $|e(-)|/|e(+)|$ by k with

$$k \approx |\Delta E|/|e(+)| \qquad (39)$$

there results for case 1

$$\Delta E_g > (k + 1)|e(+)| \qquad (40)$$

and for case 2

$$\Delta E_g > \Delta E \qquad (41)$$

In these cases the effective working bias has been assumed to be E_{g0}.

Figure 4 shows that the decrease of ΔE_g is due to the flow of grid current on the side of more positive E_g and to the decrease in anode current i_T on the other side. The anode current limitation for positive E_g is advantageous. Supplementing the ΔE_a curve for the equilibrium conditions there generally exists a dynamic $(\Delta E_a)_d$ curve corresponding to a minimum v_p reached during the transient I when the grid voltage of the tube has swung momentarily to a higher positive value.

The characteristic ratio $\Delta E_a/\Delta E_g$ varies appreciably with E_k, and to the apparent optimum value E_{g0} for E_g (E_{k0} for E_k) there corresponds a poor value of $\Delta E_a/\Delta E_g$. Although it is disadvantageous to obtain limiting by means of grid current, because so doing decreases the speed of the rising transient condition II, it nevertheless provides a means of making the circuit insensitive to positive pulses and other grid voltage variations that could be amplified otherwise by the conducting tube and transmitted to the following unit as negative pulses. Saturation of anode current by the effect of R_1

reduces the amplitude of such false trigger signals. The working value of E_g is thus adjusted for a slightly lower value than E_{g0}.

In the case of negative and positive input pulses, the stability requires relatively small pulse amplitudes, while fast switching with sloping pulse fronts requires large amplitudes. Differentiating types of couplings between units can improve the amplitude discrimination by enhancing the pulses that have the steepest fronts, which is, in general, the case for the negative ones, as follows from the time constants involved in the two transient conditions. These difficulties are almost entirely eliminated with diode coupling.

By means of the diagram of Fig. 4, the effects of circuit asymmetry can be investigated. For a practical case, two curves must be traced for ΔE_g and ΔE_a, each corresponding to the anode circuit of one tube and the grid circuit of the other, because the two half-circuits, heretofore considered to be identical, are rarely so in reality. The common setting range for E_k thus becomes smaller in general than the ideal range for a symmetrical circuit. The displacement between the two ΔE_g curves, as well as their difference in height and form, gives a means for measuring the asymmetry of the circuit.

If the tolerance percentages to be provided for different components and tubes are to be evaluated, ΔE_g curves can be drawn, for instance, for the most adverse combination, and the resulting adjustment range, as well as the equilibrium factors, and the variations to be expected in the supply voltage studied to find if the proposed tolerances can be accepted or not.

Resolving Time

The resolving time depends ultimately on the equilibrium potentials and the values of the circuit components. The resolving time is different for counting of separate groups of double, triple, . . . or periodically recurring pulses.

A voltage step following a preceding step after a short interval τ can retrigger the scale unit before the recovery to the equilibrium is completed. The shorter τ the greater the divergence from the equilibrium conditions at the start of the following cycle; this effect is cumulative. The shortest interval τ_{min} for which the scale unit resolves two successive pulses with identical characteristics is called the resolving time for pulse pairs. The resolving time, or resolution, could be defined as the time taken by the grid of the initially nonconducting tube to reach a given bias corresponding to a sufficient anode voltage drop so as to provide an output pulse sufficient for the detection of the transfer. To this interval it might be necessary to add the time for switching. However, in any case, the resolution is determined experimentally.

The resolving power for closely spaced pairs of pulses depends primarily upon the switching and transfer, while the resolving power for periodically recurring pulses is determined by the recovery time, because in this case the recovery to equilibrium values has to be almost complete.

Reviewing the influence of the different factors upon the resolving time, we can draw the following conclusions:

For greatest resolution, symmetrical units, carefully adjusted switching with rectangular voltage steps (relative to the intrinsic time constants of the units) and well filtered and stabilized supply sources are necessary. Small grid bases and limited grid voltage excursions (done automatically by grid current and possibly by diodes for negative swings) are advantageous.

The time delay in initiating the regenerative transfer cycle depends on the steepness of the switching voltage step, on the equilibrium values of the

grid potentials, on the gain of the stages, on $\Delta E_a/\Delta E_g$, on the intrinsic time constants of the unit, and in particular on some components such as R_1 and C_s. To decrease this time delay, tubes having high transconductances, high $\Delta E_a/\Delta E_g$, the smallest possible circuit capacitances (except C_s, which must be several times greater than the tube capacitances) and low ΔE_g are advantageous. The problem can be reduced to a greater extent to the choice of a tube. Actually possible resolving times range from 10^{-7} towards 10^{-8} second. Transit time effects could thus be neglected, except for the switching. Diode coupling, even with germanium crystal diodes, does not eliminate all the capacitive loading on the preceding unit, no series capacitor being used.

The lowest static tube resistances, and also the dynamic plate resistances, are obtained with low-μ triodes, but these tubes exhibit very appreciable grid-anode capacitances and large grid bases, in contrast with the special high-frequency triodes and pentodes. If the input coupling does not introduce appreciable supplementary capacitive coupling with inhibiting character, pentodes can be used, their greater dynamic resistance slowing down the speed of the transient condition I but, if the transmission delay is small, this does not affect the resolving time and results in a slightly longer interval for the fall of $v(t)$; the longer rise time remains approximately unaffected.

Reliable, fast triggering requires small grid bases and high $\Delta E_a/\Delta E_g$.

The transient response to a step voltage input of the anode circuit can be improved as in video amplification by introducing series inductance compensation. The quality factor $Q = (1/R_1)(L/C_a)^{1/2}$ may not exceed values of 0.6 or 0.75 if damped oscillations are to be avoided.

If the preceding scale unit has a better resolution than the following one, the switching of this last unit is facilitated. Likewise, it is desirable that the input circuit preceding the scaler deliver uniform pulses with suitable width. The coupling between units has been considered earlier in this paper. The new tubes with small grid bases for the control and suppressor grids can be used in a circuit with separate switching and internal cross coupling.

Cathode Self-Biasing

Instead of using two supply sources, only one need be used if cathode self-biasing is obtained by a cathode resistor R_c shunted by a capacitor C_c. Such self-biasing eliminates the effects of nonproportional variations in the two supplies. If the cathode potential is sufficiently stabilized by the large shunt capacitance or by using a common cathode resistor for several units (as is done in some types of ring arrangements) the anode load for the transient conditions remains the same as with two separate supplies; that is, it is R_1. However, for the equilibrium conditions the tube current depends on $R_1 + R_c$ and can be found from the i_p versus v_p characteristic by drawing a line with a slope equal to the reciprocal of $R_1 + R_c$.

The analysis of the first portions of this paper can be applied to the case of self-bias, and the value of the bias resistor necessary to realize a cathode bias E_c (instead of E_k), using the relation $E_c = R_c i_c = R_c(i_T + i_g + i_0)$, can be calculated as a function of E_g, the effective bias, by

$$R_c = \left[\frac{1}{i_c(R_1 + R_2 + R_3 + 2R_4)}\right] \{[E_0 - (R_1 + R_2)i_c](R_3 + 2R_4) - i_B R_4(R_1 + R_2)\} + E_c/i_c \quad \text{for} \quad i_0 = 0 \quad (42)$$

in the case of a unit using triode tubes. For pentodes the screen grid current has to be considered, and leads to smaller values of R_c. Stabilized screen-grid potentials are necessary. The

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cathode bias E_c is not as constant as E_k, but the slow bias changes can help to stabilize the unit.

In the case of supplementary cathode feedback, the effective grid bases of the tubes are changed and the triggering is thus further complicated. Using a common R_c for a group of tubes reduces this feedback and in some circuits no shunt capacitor C_c is provided to permit the application of the trigger pulse to the cathode.

Scales-of-*N* Systems

Among the scales-of-N, the decimal scales take an important place. Various investigators have treated the decimal scale in various ways, such as using scale-of-2 units in series or in a closed-ring combination. In the series type, pulses can be fed back to previous units to bring, for instance, a scale-of-8 to its initial state after only 5 incoming pulses. A scale-of-10 can then be obtained by assembling a scale-of-5 with a scale-of-2, this last being put ahead of the other. Various ring arrangements have been described in the literature. An arrangement using a gate controlled scale unit to obtain a decimal scale with a combination of a scale-of-2 and a scale-of-4 unit has also been described, as well as a decimal scale with diode switching elements, and diode switching to convert a scale-of-16 into a scale-of-10.

An interesting realization was the generalization of the scale-of-2 circuit into a scale-of-N with N tubes. The stability of generalized scale circuits with N equilibrium conditions can also be investigated by a generalized diagram of Fig. 4 with N of the ΔE_g curves. The possibility of there being greater asymmetry can be neutralized partly by grid current limiting.

For fast decimal scales, special ring type arrangements seem well suited, while series types can always be used either with capacitive or diode couplings, but give a scaling ratio 2^N. The details of all these circuit combinations can be found in the literature listed at the close of this paper. The particular advantages or disadvantages of each one are evident from the previous considerations.

Design Procedure

The deadtime of a radiation counter determines the maximum needed resolving power of the scaler. Knowledge of the maximum mean pulse rate per second that is to be counted with random pulse distribution in time and of the insensitive time interval of the register after a count has been recorded (0.1 to 0.01 sec) permits one to determine the total scaling factor N and the resolving time of the first scale unit, if a given counting loss, say 1%, is acceptable and assuming that the scaling apparatus can be characterized by a single resolving time.

The required resolving time of successive scale units can be determined by probability considerations so as to limit the total scaling factor N.

Dynamic and static asymmetries, changing with time in general, disturbing effects of imperfect switching, of positive pulses, and other disturbances can be overcome by careful design of the equilibrium conditions, the intrinsic time constants and the couplings between units.

No rigorous formulas can be given for the resolving time, even for approximate considerations; only knowledge of the important factors with which the designer must deal and sufficient theoretical understanding of the operation are available. Knowledge of the effects resulting from changes in the components can help in guiding the experimental work.

The choice of a tube depends largely on the needed resolution. The values of the resistors are not critical, but a compromise has to be made for every

unit between resolution and stability, the former being the primary factor in the first unit and the latter in the last unit. Once a tube has been chosen, conservative ratings should be used; thus the supply voltages, E_a or E_{g_2} are known, as are also the tube characteristics. Expressing R_2 by wR_1 and R_3 by zR_1, one can draw curves giving $\Delta E_a/\Delta E_g$ and ΔE_g as functions of R_1 for constant w and z, and for constant $w + z$ but different w/z values. Decreasing R_1 results in a decrease of ΔE_g and an increase of $\Delta E_a/\Delta E_g$, in the case of triodes and pentodes and with w and z constant when w/z equals about 2, for instance. Representative component values for a scale-of-2 circuit with two 6AG5 tubes are, for example: $R_1 = 5{,}000$; $R_2 = 39{,}000$; $R_3 = 22{,}000$; $C_s = 30$ $\mu\mu$f; $R_c = 5{,}000$ to 10,000 (adjustable); $C_c = 0.1$ μf or greater; $E_0 = 275$ volts; diode or capacitive input coupling; trigger pulse width of the order of tenths of 10^{-7} sec for fast scaling; $E_{g2} = 150 - E_c$ volts.

Sufficient attention has to be paid to the auxiliary circuits. The input circuit has to amplify the pulses to a sufficient level; amplitude limiting, making the pulse front steeper and the width shorter are useful. Monostable circuits of the Schmitt-trigger type can be used for pulse height discrimination and for making the pulses more uniform. The designer should be familiar with special circuits and techniques to obtain the best results with the simplest arrangements.

For driving the register quickly, an output circuit is needed that delivers almost rectangular pulses of current of well-adjusted width into the relay. Pulses can be lengthened by integrating *R-C* networks used for interstage coupling, while heavy current pulse sources with high internal resistance require an overbiased output tube with high anode voltage and driven by large grid pulses with grid current limitation.

Generally, electronically stabilized power supplies are used for the auxiliary circuits of the input amplifier and pulse former, and also for the scale units, although triode scalers can operate satisfactorily on common power supplies by utilizing a general automatic bias, but these scalers are more sensitive to stray pulses carried by the lines. Pentode scalers require stabilized screen grid voltage.

Interpolation circuits using neon tubes or microammeters do not provide any difficulty and are profusely treated in the literature. Meter indication of the count with decimal scales requires more adjustments than neon interpolation systems.

* * *

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Broad and Narrow Beam Attenuation of 500-1400 Kv X-rays in Lead and Concrete

Report on X-ray shielding investigations, together with attenuation curves for use in designing X-ray protection

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NUMEROUS PAPERS over the past ten years have dealt with X-ray protection in the range from 500 to 2000 kv (*1*). The data from these papers vary somewhat because the conditions of the experiments were not always the same and could not readily be correlated. Part of this variance has been attributed to differences in the high voltage wave form and inherent filtration for the various experimental arrangements. Preliminary data (*1*) have indicated that the size of the irradiated area of the barrier may also be an important variable. The magnitude and limits for this variable have not, however, been explored quantitatively. The present report will deal with X-ray beams of various sizes produced by direct-current potentials of 500, 600, 800, 1000 and 1400 kv with a transmission target. Barriers of lead and concrete will be considered. Concrete has been generally accepted in the energy range above about 500 kv where space is not important because it is structurally self-supporting and relatively inexpensive. However, for applications requiring a minimum of thickness for a given protection, lead is still the most popular.

In the voltage range under consideration, X-rays are principally absorbed by the photoelectric and the Compton processes since pair production is still relatively unimportant, even in lead for 1400 kv. All of the photoelectric absorption and that part of the energy transferred to the Compton electrons are considered to be truly absorbed since the electrons so produced have small likelihood of producing another X-ray photon. The part of the energy given to the scattered photon leaves the site of the encounter in a different direction from that of the incident photon. The amount of this energy retained by the scattered photon decreases with increase of the angle between the scattered and incident photons. Thus, if the beam is of small cross section, the scattered photons leave the incident bundle and will not be measured. If, however, the beam is of considerable width, the photons scattered from the sides of the beam may enter a measuring volume situated near the center of the beam. The apparent attenuation of the beam, measured by the reduction in dosage rate in the barrier, may thus be greatly influenced by the inclusion of this scattered radiation.

One may think of the ionization produced in the ionization chamber placed on the far side of a protective barrier as being due to two different sources of radiation. (1) Part of the radiation comes directly from the target of the X-ray tube. (The target is essentially a point source for all practical dimensions used in protective studies.) (2)

The remainder of the measured dosage may come from a distributed source composed of the entire irradiated volume of the protective barrier. Several factors serve to limit the volume which acts as this secondary source. The length of the incident plus the scattered photon path in the barrier will be greater for oblique rays and therefore obliquely incident photons have a greater probability of being absorbed. In addition, the angle between these incident and scattered photons must be larger and therefore the scattered photon energy will be smaller. The latter factor, depending upon the atomic number of the protective barrier, may also increase the probability of true absorption. In the X-ray range here considered, this factor is not important for concrete but serves to limit the practical dimensions of the virtual source when lead barriers are used.

Another factor producing differences between measurements made with and without scattering has recently been described (*2*). It was shown that air ionization chambers are more sensitive to photons of energies below 70 kv than above. For increasing thickness of barrier an equilibrium is soon established so that as much of the low energy radiation is absorbed as is created. As a result of this quality-dependent chamber sensitivity, one obtains an increase of dosage rate in protective barriers of low atomic number, such as concrete, where this low energy radiation is not strongly absorbed. The attenuation curves are thus convex upward for small barrier thicknesses. On the other hand, for barriers of high atomic number such as lead, this effect is not observable since the low energy radiations are strongly absorbed in the barrier.

As can be easily seen from the above discussion, different experimental conditions may influence considerably the attenuation curve obtained. Two limiting conditions are thus defined for the work to be reported here. A narrow beam attenuation curve shall be understood to be one where only a negligible amount of the scattered radiation from the barrier is measured in the ionization chamber. Practically, this condition amounts to having the irradiated area on the barrier subtend a small angle at the chamber. This condition may be verified experimentally by an inverse square check of the radiation received in the chamber. If the inverse square law is found to hold experimentally, with fixed position of the target and barrier but with variations of the target-to-chamber distance, then the contribution of scattered radiation from the barrier source is negligible.

If, on increasing the irradiated area of the barrier—with a fixed position of the chamber, target, and barrier—no increase in dosage rate is observed, the broad beam conditions prevail. This condition is, of course, only unique for that particular barrier-to-chamber distance. The above qualitative considerations indicate that the irradiated area required to fulfill broad beam conditions will be larger for larger barrier-to-chamber distances. The requisite area may be reduced by shorter target-to-barrier distances and smaller chamber volumes.

Since some scattered radiation is measured by the chamber under broad beam conditions but none is measured for narrow-beam conditions, the effective absorption coefficient must be different for the two conditions. The effective absorption coefficient is, however, proportional to the slope of the attenuation curve. Attenuation curves that include different amounts of scattered radiation in their determination should therefore have different slopes.

Experimental Arrangement

The high voltage generator and tube have been previously described (*3*). Fig. 1 shows the experimental arrangement for beam collimation and for

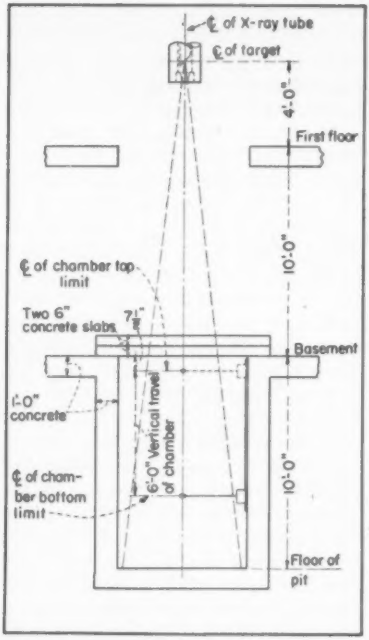

FIG. 1. Experimental arrangement for collimating the beam and for dosage measurement

dosage measurement. The filtration inherent in the X-ray tube was approximately 2.8 mm tungsten plus 2.8 mm copper plus 2.1 mm brass plus 18.7 mm water for the center of the beam. The target protective housing consisted of a double-walled steel tank filled with lead shot to a thickness of approximately 6 inches, and a 6-inch thick solid lead diaphragm. Three diaphragms of different apertures were used in the course of the experiments. They gave irradiated areas at the basement floor level whose diameters were approximately 13, 26 and 37 inches respectively. These dimensions were dictated on the lower end by the requirement of uniform irradiation of the chamber and on the upper end by a desire to minimize scattering from the pit walls.

Figure 2 shows a view of the pit in which the radiation measurements were made. The ionization chamber was connected to an evacuated cylinder housing an FP54 electrometer tube and a selection of resistors, and could be moved by remote control both in azimuth and in elevation within the pit. (The chamber actually used had about $\frac{1}{25}$ the volume of the one shown in Fig. 2.) Remote switches controlled, and indicators defined, the position of the chamber in the pit, the resistor being used, and the grid resistor voltage. The latter two figures together with the volume of the chamber and the temperature and pressure of the air served to determine the dosage rate. The chamber calibration, which was determined from the value of the grid resistor, the grid voltage and the mass of air in the chamber, agrees to within 5% with that obtained experimentally with a standard radium source. By controlling the voltage and the current of the X-ray tube to within 0.1%, the X-ray dosage was found to be constant to 3%. A good share of this fluctuation in output could be attributed to random focal spot motion. It was not considered excessive for this purpose.

For narrow beam conditions, the absorbers were placed directly below the shield diaphragm. The chamber-to absorber distance could thus be varied from approximately 10 to 16 feet. The irradiated area of the samples was not more than 3 inches in diameter.

In testing for broad beam conditions the absorbers were laid directly over the top of the pit with an overlap of approximately one foot all around the lip. The concrete samples were in one piece, either 8 ft × 8 ft × 6 in. or 8 ft × 8 ft × 3 in. Lead samples were made of 2 ft × 8 ft × ⅛ in. thick strips. Parallel strips covered the whole surface of the pit aperture in ⅛ in. thick layers. An overlap of at least ¼ in. was provided at each joint. Lap joints were staggered

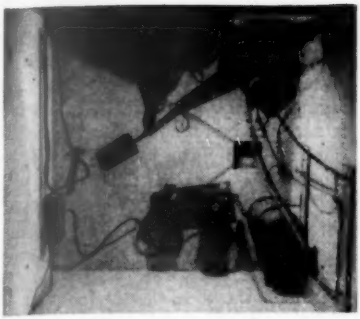

FIG. 2. View of pit where radiation measurements were made

in adjacent layers but none of the joints came closer than 9 in. to a line through the chamber and target. This lead, being quite flexible, required additional support. The pit aperture was reduced by placing plyboard on the basement floor extending over the pit. An unsupported area of lead 3 ft square was obtained in the center of the aperture. (This area was found to be adequate for broad beam conditions with concrete. Smaller dimensions were expected and obtained for lead.)

The large concrete blocks were each weighed to an accuracy of 10 pounds. Corrections were made for known air holes and reinforcing iron around the unexposed edges. Thicknesses of each slab, measured at a number of distributed points, were found to deviate by no more than $\frac{1}{8}$ in. from their mean value. This mean thickness together with the length, the width and the corrected weight served to determine the average density. The mean of five additional thickness measurements obtained in the vicinity of the X-ray irradiated area was then corrected to correspond to a specific gravity of 147 pounds per cubic foot (2.35 grams per cc). The narrow beam concrete blocks were those previously used (*4*). Accuracy of the concrete dimension measurements was estimated to be within 2%.

Approximately 300 measurements of thickness of the lead strips indicated maximum deviation from the mean of the order of $\pm 4\%$.

All attenuation curves were obtained for a $7\frac{1}{2}$-in. chamber-to-barrier distance. This distance was a practical lower limit for our equipment. However, personnel are usually not located closer than $7\frac{1}{2}$ in. to the protective barrier in most medical X-ray installations. The target-to-chamber distance was thus $175\frac{1}{2}$ in.

Results

In order to evaluate this experiment properly, it was necessary first to investigate the extraneous scattering. Evidence of the lack of scattering without absorber may be obtained by observing the dosage rate at different distances from the target. The inverse square law may be used to reduce these dosage rates to a common distance. The variation of the values, so computed, is a measure of the amount of scattering present. Figure 7A indicates the magnitude of the scattering. It is seen that, with no absorber in place and for the two smaller diaphragms, dosage rates computed back to a fixed distance (1 meter) by the inverse square law remain essentially constant for large variations of the target-to-chamber distance. With the largest diaphragm the main beam actually begins to strike the side walls about halfway down the pit. The resultant scattering from the walls may contribute to the dosage rates measured in the center of the beam. Since the scattering is most important in the forward direction, some increase in the measured radiation should be obtained for chamber positions below the mid-depth of the pit. The experimental evidence verifies this qualitative prediction. Figure 7A indicates that the contribution of scattering is about 5% of the main beam at a distance of 80 inches below the lip of the pit.

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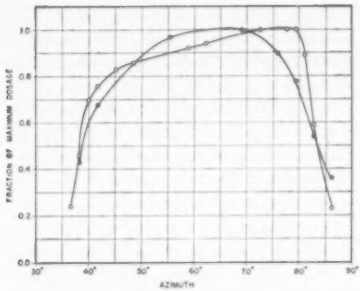

FIG. 3. Variation of dosage rate across X-ray beam for an irradiated area of approximately 37-inch diameter. The open circles were obtained with no barrier. The filled circles were obtained with a 6-inch thick concrete absorber in place

Scattered radiation will, of course, be measured with an absorber over the pit. The lack of extraneous scattering from the pit walls may be determined by measuring the radiation very near to the wall. If the radiation measured near to the wall is a small part of that in the center of the beam, any contribution received at the center of the beam from the wall may be negligible. In Fig. 3 the pit walls correspond to angles of approximately −5° and 95°. The experimental results indicate that the dosage rate is rapidly decreasing as the walls are approached. The amount of radiation scattered from the nearer wall to the center of the beam is thus negligible.

Figure 3 also indicates other interesting items. The sloped central portion of the azimuth curve without absorber has been discussed previously in the literature (*5*). It may be attributed to change of the inherent filtration with angle. The asymmetry results from having the target set at 45 degrees to the emergent beam. Large azimuth angles on this figure correspond to least inherent filtration. The figure also indicates that the presence of an absorber tends to sharpen the main peak but to increase the dosage rate near the foot of the curves. The first factor may be attributed to diminution of the beam by larger thicknesses of material at points different from the normal to the absorber. The second factor may be attributed to the radiation scattered out of the confines of the original beam.

It was found that each diaphragm gave a different apparent tube output. This increase in dosage rate with diaphragm size was attributed to spread of the focal spot. In order to show more clearly the effect of beam size on the attenuation curves, all dosage rates for a given diaphragm and kilovoltage have been reduced by the ratio of the apparent tube outputs—with zero absorber—for that diaphragm and for the smallest diaphragm. All four sets of curves for a given voltage thus pass through the same zero absorber point.

Figure 4 shows the experimental attenuation curves for lead. The lower curve at each potential is for narrow beam conditions. There was no important change in the data for irradiated areas greater than 13 in. in diameter. The actual deviation of the dosage rate for variation of the diaphragm was of the same order as the experimental error. There is, however, an interesting change in the difference between narrow and broad beam absorption curves with potential producing the X-rays. In agreement with the qualitative predictions, this difference becomes more important for large photon energies since the scattered photons are not so readily absorbed photoelectrically.

Figures 5 and 6 show the attenuation curves for concrete. For each generator potential, the lowest curve is for narrow beam conditions, that is, when a negligible amount of the dosage is due to scattering from the absorber. The difference between successive curves with narrow beam, 13, 26 and 37 in. irradiated diameter, indicate the magni-

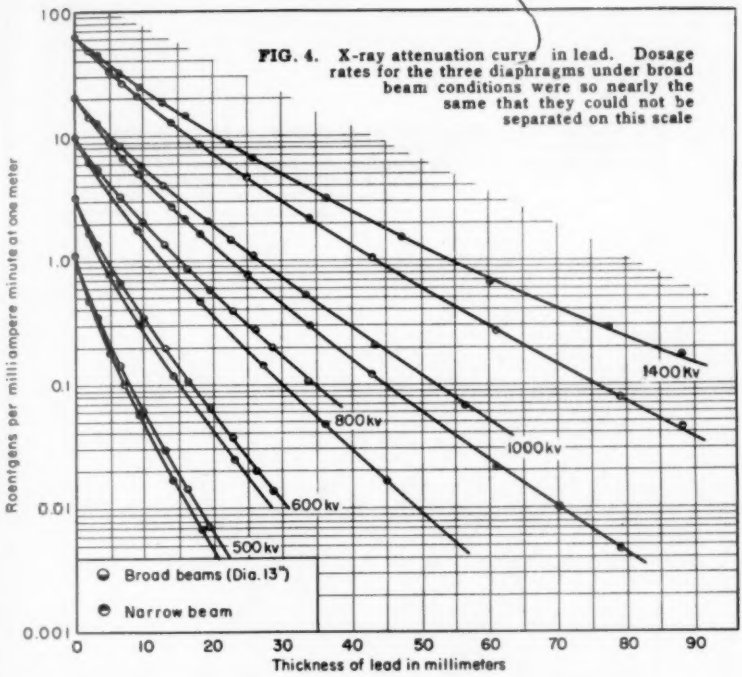

FIG. 4. X-ray attenuation curve in lead. Dosage rates for the three diaphragms under broad beam conditions were so nearly the same that they could not be separated on this scale

tude of the scattering from the corresponding ring of barrier. It is evident that the scattered photons from the successive outer rings contribute less and less to the dosage rate measured on the axis of the beam. Because of the small change in dosage rate between the 26 and 37-in. beams and because of the rapidly decreasing contribution of scattering with beam size, the 37-in. diameter beam in concrete has been assumed for all practical purposes to correspond to broad beam conditions under the experimental arrangement described above.

For comparison with data obtained from a resonance X-ray generator, two experimental points from Singer, Braestrup, and Wyckoff (SBW) (*1*) have been included on Fig. 6. These were obtained with a two-million-volt resonance-type unit operating at one million volts peak and giving an irradiated area of approximately 4½ by 7 ft. The target-to-chamber distances were approximately 8 and 9 feet. These data have been corrected as nearly as possible to the experimental conditions used for our new data. The effect of the wave form on the X-ray output and the effect of the shorter target-barrier distance on the amount of the scattering measured in protection studies cannot be rigorously determined with our present knowledge. One may say, however, that the target current flows appreciably only when the alternating voltage peak is above 800 kv. The effective potential should therefore be somewhere between 800 and 1000 kv.

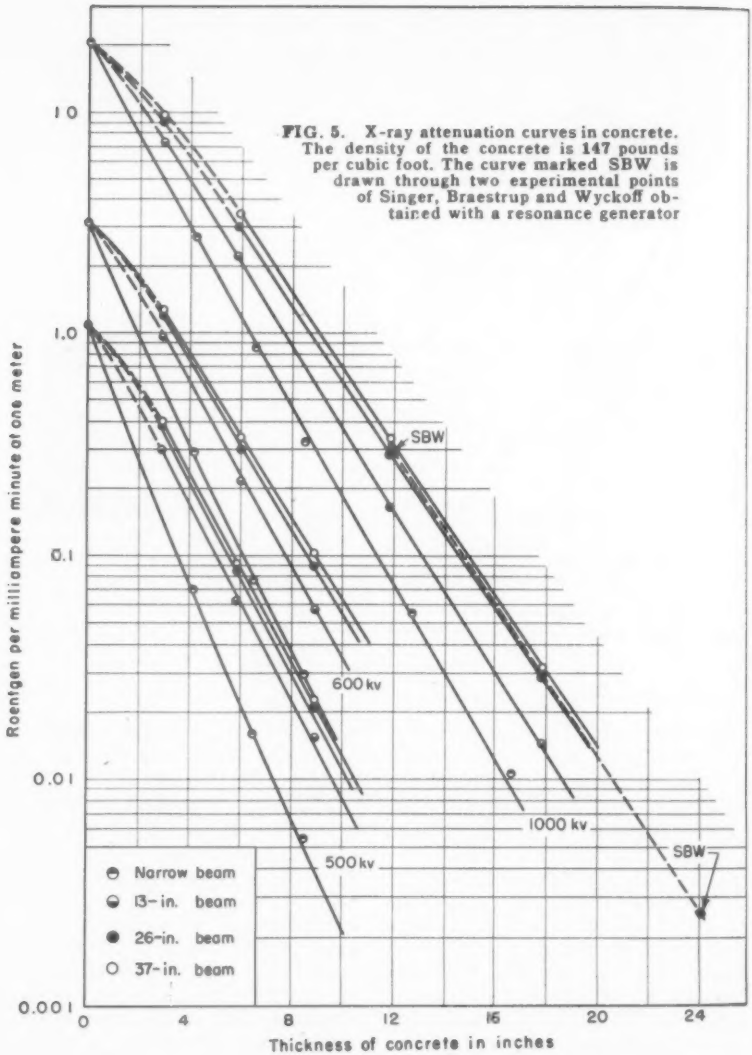

FIG. 5. X-ray attenuation curves in concrete. The density of the concrete is 147 pounds per cubic foot. The curve marked SBW is drawn through two experimental points of Singer, Braestrup and Wyckoff obtained with a resonance generator

The slope of an attenuation curve is often taken as a measure of the effective potential of the X-rays. The points from SBW give a line whose slope is midway between that reported here for 800 and 1000 kv. The results are thus in qualitative agreement.

There is evidence, in the lead as well as in the concrete curves, of a reduction in the slope of the attenuation curve

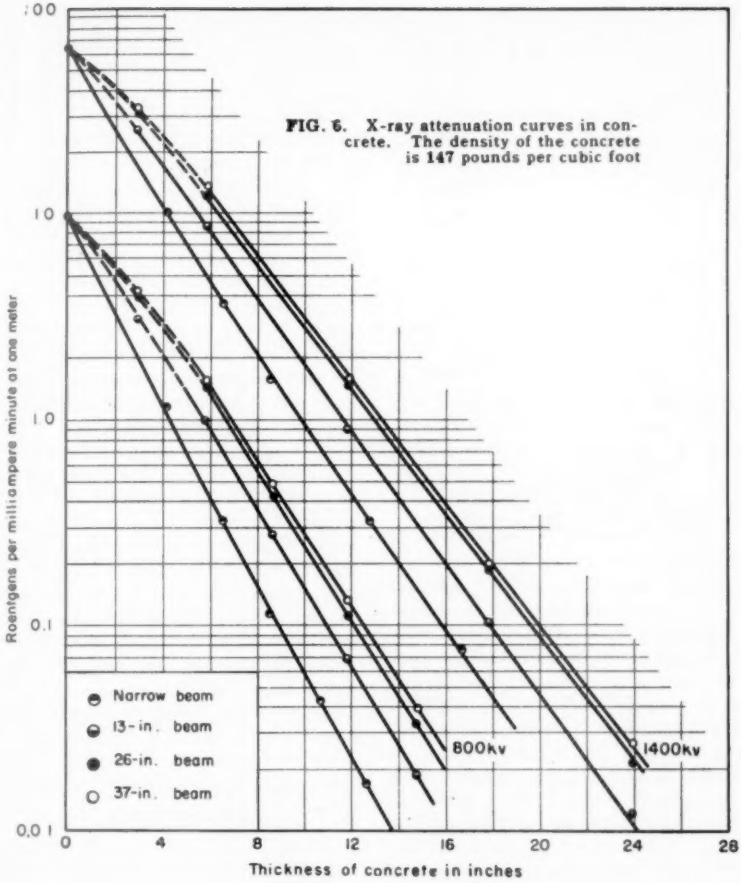

FIG. 6. X-ray attenuation curves in concrete. The density of the concrete is 147 pounds per cubic foot

with irradiated area. This effect is especially pronounced in the change from narrow beam to 13-in. diameter beam. There is also evidence in concrete, but not in lead, of the low-energy scattered radiation. Both of these items tend to increase the barrier thickness requirements for broad beam over those for narrow beam.

Figure 7, for data taken at 1000 kv, shows the importance of barrier-to-chamber distances. These curves were obtained by varying the elevation of the chamber in the pit. Figure 7B is for a lead absorber placed over the pit. The three diaphragms all give essentially the same dosage rate at a distance of 7½ in. below the absorber. Broad beam conditions were therefore obtained at this position for an irradiated area of 13 in. diameter. As the barrier-to-chamber distance is increased,

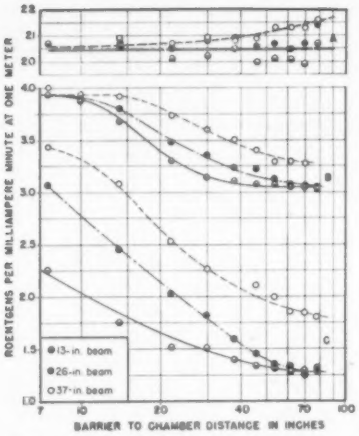

FIG. 7. Samples of the variation of X-ray dosage with distance from the lip of the pit (1000 kv):
A) with no absorber in the beam
B) with 12.9 mm of lead over the pit
C) with 5.8 inches of concrete over the pit

different diaphragms do not give the same dosage. Broad beam conditions, therefore, do not exist in this intermediate region for the diaphragms used. At very large distances, the dosage rates appear to become constant. This condition corresponds to the requirements for narrow beam. As would be expected, the distance from the barrier for narrow beam conditions increases with the size of the irradiated area. After correction for scattering, the dosage rate of the largest beam also agrees with that of the other beams at a distance of 78 in. Moreover, this constant dosage rate agrees with that obtained for the narrow beam curves of Fig. 4. For the concrete sample indicated (Fig. 7C), it appears that the two smaller diaphragms approach narrow beam conditions for a chamber-to-barrier distance of the order of 55 to 78 in. The dosage rate is here constant (1.3) and in agreement with the narrow beam curve of Fig. 5, which also gives a value of 1.3 r per ma min at 1 meter.

Conclusions

Because of the small irradiated areas required for broad beam conditions in lead, the broad beam attenuation curves should be used for nearly all cases where lead barriers are considered in this voltage range. The extra thickness of lead required for broad beam conditions over that for narrow beam varies rapidly with X-ray tube potential. This extra thickness requirement varies from approximately 10% at 500 kv to 25% at 1400 kv.

For concrete protective barriers the difference between narrow and broad beam thickness requirements is of the order of 1.5 to 2 half-value layers depending upon the portion and kilovoltage of the curves considered. If the irradiated area of the barrier is not more than 3 feet in diameter and if all personnel are restricted to distances larger than 10 feet from the barrier then narrow beam attenuation curves may be used in designing X-ray protection. Such restrictions are not usually feasible, however, because of space limitations. In addition, the cost of requiring the extra space may be larger than the saving in barrier cost. For the majority of X-ray installation designs, therefore, the broad beam attenuation curves should be used.

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Volume I, No. 1. Nuclear Science Abstracts. (These abstracts cover AECD 2024–2064 and also articles appearing in both domestic and foreign publications, pertaining to atomic energy.) .35

NUCLEONIC EVENTS

WESTINGHOUSE FORMS ATOMIC POWER DIVISION

The Westinghouse Electric Corporation has formed an atomic power division which will concentrate solely on the harnessing of nuclear energy for the production of useful power, it was disclosed last month by Gwilym A. Price, Westinghouse president.

Emphasizing the importance of atomic energy in the future of the nation's electrical industry, Mr. Price declared:

"The use of nuclear energy as a source of power is recognized as a possibility which may profoundly affect the development, design, and application of many lines of electrical equipment in the years ahead.

"The atomic power division will be available to undertake atomic energy projects for the United States government as well as to carry on independent studies. It will conduct research, development, engineering, and any necessary associated construction."

The new division, he added, will work closely with the Westinghouse Research Laboratories and with other divisions of the company so as to benefit from their knowledge, experience, and facilities. Its location and other details of organization will be announced later.

Manager of the atomic power division, Mr. Price announced, will be Charles H. Weaver, a young Westinghouse executive who has recently served as industrial manager of the company's central district with headquarters in Pittsburgh.

A native of Philadelphia, Mr. Weaver was graduated from the University of Pennsylvania in 1936 with the degree of bachelor of science in electrical engineering, and joined Westinghouse that same year. During the war years he served as manager of the Westinghouse marine department which, from 1945 on, included aviation activities also. This department handled a large share of the company's wartime production contracts.

Among his other professional affiliations, Mr. Weaver is a member of the Society of Naval Architects and Marine Engineers, the American Society of Naval Engineers, the American Institute of Electrical Engineers, and the Engineers Society of Western Pennsylvania.

SITE SELECTED FOR KNOLLS POWER REACTOR

Selection of a site for the new experimental atomic power plant to be built as part of the Knolls Atomic Power Laboratory has been announced by the Atomic Energy Commission. Located in Saratoga County, New York, the 4,500 acres of land, upon which preliminary construction work will begin this fall, are near West Milton, 10 miles west of Saratoga Springs and 15 miles northeast of Amsterdam. The site is about 18 miles north of the Knolls Atomic Power Laboratory, operated for the AEC by the General Electric Company at Schenectady.

According to C. G. Suits, vice president and director of research for GE, the nuclear reactor will be quite different from the production reactors at the Hanford Works in Washington. The Hanford plant, also operated by GE, was built during the war for the sole purpose of making plutonium for military purposes and generates no useful power.

The new Knolls reactor is one of two

now being designed especially for the study of high-temperature operation and the production of power. A different type of reactor but for a similar purpose is planned at Argonne National Laboratory near Chicago. The design of both these reactors is directed to the problem of power generation by nuclear fission but by different methods, and both are expected to yield important data leading ultimately to the design of reactors which will produce power on a practical scale. The prediction has been made that the Knolls pile might be in operation three years after the start of construction.

CORNELL DEDICATES NUCLEAR LABORATORY

The new $2,000,000 Laboratory of Nuclear Studies at Cornell University, Ithaca, N. Y., was formally opened last month. The main laboratory building and an adjacent structure housing a 300-Mev synchrotron was dedicated as part of the celebration of the eightieth anniversary of the opening of the university.

The Nuclear Laboratory Building is 160 feet long and 48 feet wide, with a useful floor area of 30,000 square feet. The Synchrotron Laboratory Building, connected to the main structure by personnel and service tunnels, is 70 feet long, 68 feet wide and 24 feet high.

The main laboratory contains 16 single and three double laboratories, four radiochemistry laboratories, two machine shops, an electronics shop, stockrooms containing some 3,000 items, synchrotron control and detector rooms, and a roof deck for cosmic-ray research. Its other facilities include conference, seminar, recreation and shower rooms, two darkrooms, and a kitchen.

The cosmic-ray laboratory, now being built on the roof deck and planned to measure 10 by 60 feet, will provide facilities for housing recording equipment for cosmic-ray experiments. Other roof space will be available for setting up Geiger-Müller counters to measure extensive cosmic-ray showers.

Much of the research work of the laboratory will center around the synchrotron, now undergoing preliminary testing in its adjoining building. The machine, 13 feet in diameter and weighing 85 tons, will accelerate electrons to an energy of 300 million electron volts. Financial support for construction of the machine has been provided by the Office of Naval Research.

Cosmic-ray experiments will be undertaken both at the laboratory and at the Inter-University High-Altitude Laboratory in Colorado. The laboratory also has initiated a program of providing technical assistance to other university departments in their use of radioactive isotopes for tracer work.

The facilities of the new Laboratory of Nuclear Studies will be used by a staff of 59 which includes 18 faculty members, 24 other full-time staff members, 11 graduate research assistants and six part-time or temporary technicians.

In charge of the laboratory is Robert R. Wilson, who has been in direct charge of the final design of the laboratory buildings and their equipment, including the synchrotron. Dr. Wilson came to Cornell from Harvard where he prepared plans for a new cyclotron. A graduate of the University of California, with a Ph.D. from the same institution, he was in charge of the experimental work of the Princeton branch of the atomic energy project in 1941–43 and later was head of the Division of Experimental Physics at the Los Alamos Laboratory of the Manhattan District.

REACTOR MEETING HELD AT ARGONNE LABORATORY

A meeting concerned with reactors was held last month at the DuPage County Laboratory of the Argonne National Laboratory and was attended by the following people: E. B. Ashcraft,

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E. Blizard, L. P. Hunter, J. A. Lane, M. M. Mann, and A. M. Weinberg, of the Oak Ridge National Laboratory; H. Brooks and J. P. Howe, Knolls Atomic Power Laboratory, General Electric Company, Schenectady, New York; E. Fermi, Institute for Nuclear Studies, University of Chicago; D. A. Gurinsky, Brookhaven National Laboratory; David B. Hall, Los Alamos Scientific Laboratory; A. R. Kauffmann, Massachusetts Institute of Technology; H. W. Russell, Battelle Memorial Institute; C. Starr, North American Aviation, Inc.; C. W. J. Wende, Hanford Engineer Works; E. P. Wigner, Princeton University; George Weil, U. S. Atomic Energy Commission; M. B. Rodin, and S. M. Skinner of the Office of Chicago Directed Operations; and H. Etherington, Frank Foote, J. R. Huffman, H. V. Lichtenberger, N. Hilberry, O. C. Simpson, S. Untermyer, and W. H. Zinn of the Argonne National Laboratory.

SHIELDING SYMPOSIUM HELD AT OAK RIDGE

A symposium on shielding, sponsored by the Oak Ridge National Laboratory, was held at Oak Ridge, September 27 through 30. Following is a list of the papers presented:

A Summary of Shielding Theory to Date, F. L. Friedman, Nuclear Development Associates, New York, N.Y.; Determination of Radiation Tolerance Levels, K. Z. Morgan, Health Physics Division, Oak Ridge National Laboratory; Problems and Techniques of Shielding Measurements, C. E. Clifford, Technical Division, Oak Ridge National Laboratory; Limitations Imposed on Aircraft Design by Shielding, Richard Adams, NEPA Project; Shielding Naval Power Plants, H. G. Rickover, USN, Bureau of Ships; Design of Hot Chemical Plants, Gerald Strickland, Brookhaven National Laboratory; Problems of Hot Laboratory Design, Paul C. Tompkins, Biology Division, Oak Ridge National Laboratory.

Some questions on Thermal Shields, A. M. Weinberg, Physics Division, Oak Ridge National Laboratory; Shielding Nuclear Accelerators, J. R. Dunning, Columbia University; Shielding Against Nuclear Bombs, D. K. Froman, Los Alamos Scientific Laboratory; Shielding Process and Storage Vessels from Interaction, John Morfitt, Y-12 Electromagnetic Plant, Oak Ridge; Shielding Radioisotopes for Shipment, H. E. Beddell, Oak Ridge National Laboratory and G. W. Morgan, Isotopes Division, AEC; Reflectors and Breeding Blankets, B. I. Spinrad.

The AEC and Shielding, Roger S. Warner, Division of Engineering, AEC; NEPA Shield Criteria, Robert Echols, NEPA Project; U. S. Navy, Bureau of Ships, M. A. Libbey and J. A. Kyger USN, Bureau of Ships; U. S. Navy, Bureau of Yards and Docks, R. B. Krum, USN, Bureau of Yards and Docks; U. S. Navy, Bureau of Aeronautics, Harvey Hall, USN, Bureau of Aeronautics; National Bureau of Standards, Harold O. Wyckoff, X-ray Section, National Bureau of Standards; Gaseous Diffusion Plant (K-25), Sylvan Cromer, K-25 Diffusion Plant, Oak Ridge; The RAND Project, E. H. Plesset, Project RAND.

Monsanto's Miamisburg Laboratory, J. E. Bradley, Monsanto Chemical Co., Dayton, Ohio; ORNL—Theoretical and Experimental Physics, E. P. Blizard, Physics Division, Oak Ridge National Laboratory; ORNL—Engineering and Material Studies, T. Rockwell, Technical Division, Oak Ridge National Laboratory; ORNL—Health Physics Research on Shielding, J. H. Roberson, Health Physics Division, Oak Ridge National Laboratory; The NEPA Shielding Program, Robert Echols, NEPA Project; National Bureau of Standards Shielding Research, L. S. Taylor, X-ray Section, National Bureau of Standards.

Brookhaven National Laboratory,

Marvin Fox, Brookhaven National Laboratory; Knolls Atomic Power Laboratory, Lewi Tonks, Knolls Atomic Power Laboratory; Hanford Engineer Works, John West, Hanford Engineer Works; Battelle Memorial Institute, David T. Williams, Battelle Memorial Institute; Los Alamos Scientific Laboratory, Jane Hall, Los Alamos Scientific Laboratory; Blaw-Knox Construction Company, V. A. Zora, Blaw-Knox, Chemical Plants Division, Pittsburgh, Pa.; Naval Research Laboratory, W. R. Faust, Naval Research Laboratory.

A New, Inexpensive High-Level Neutron Source, Kenneth McKenzie, University of California at Los Angeles; Hydrogenous Materials of Possible Shielding Interest, A. J. Miller, NEPA Project; Some Hydrides and Their Properties, T. R. P. Gibb, Metal Hydrides Company; Radiation Attenuation Testing at ORNL, E. P. Blizard, Physics Division, Oak Ridge National Laboratory; Special NEPA Test at ORNL Pile, Robert Coyle, NEPA Project; The "Elephant," A Unique Alpha Hood, J. L. Richmond, Monsanto Chemical Co., Dayton, Ohio; Problems Connected with Shadow Shields, Milton S. Plesset, Project RAND; More Thoughts on Shadow Shields, L. A. Ohlinger, Northrop Aircraft Co.; The Construction Angle—Examples from the Brookhaven Shield, W. N. Thompson, H. K. Ferguson Company.

Effects of Voids on Attenuation Coefficient, N. M. Smith, Physics Division, Oak Ridge National Laboratory; Shipping Containers for High Level Sources, J. A. Lane, Technical Division, Oak Ridge National Laboratory; New, Highly Hydrated Cements, A. E. Pavlish, Battelle Memorial Institute; A Review of Gamma Scattering Theory, J. O. Hirschfelder, University of Wisconsin; Gamma Attenuation Through Thick Layers of Material, G. H. Peebles, Project RAND; Gamma Scattering by Heavy Metals, Bernard Shoor, Northrop Aircraft Co.; and NACA Techniques for Calculating Neutron and Gamma Attenuation, A. R. Bobrowsky, National Advisory Committee for Aeronautics, Cleveland, Ohio.

FINAL PROGRAM ANNOUNCED FOR INSTRUMENT CONFERENCE

Final plans have been announced for the IRE-AIEE Conference on Electronic Instrumentation in Nucleonics and Medicine to be held in New York, November 29 through December 1. Of the 25 papers to be presented, 17 will be devoted to nucleonics instrumentation. In addition to the paper presentations, the Atomic Energy Commission has arranged a comprehensive display of radiation detection instruments used in the industrial, medical and biological applications of nuclear energy.

Medical instruments will be discussed on November 29. The program for the last two days, which will be devoted to nucleonics instrumentation, is as follows:

Tuesday, November 30

Presiding: G. W. Dunlap, General Electric Co., Schenectady, N. Y.

Introduction to Nucleonics Instrumentation — A. Dahl, Instrument Branch, AEC, Oak Ridge, Tenn.

Biological Requirements for Radioactive Isotope Measurements—C. A. Tobias, Jr., Donner Laboratory of Medical Physics, University of California, Berkeley, Calif. Discussion by L. Marinelli, Argonne National Laboratory, Chicago, Ill.

Geiger Counters—H. Friedman, Naval Research Laboratory, Washington, D. C.

Thin-Window Beta Counters—F. C. Henriques, Jr., Tracerlab, Inc., Boston. Mass.

Autoradiographic Technique—G. A.

Boyd, School of Medicine and Dentistry, University of Rochester, Rochester, N. Y.

Stable Isotope Measurement—D. Rittenberg, College of Physicians and Surgeons, Columbia University, New York, N. Y.

Biological Effects of Radiation and Health Protection—G. Failla, College of Physicians and Surgeons, Columbia University, New York, N. Y.

Health Protection Instrumentation—F. R. Shonka, Argonne National Laboratory, Chicago, Ill.

Wednesday, December 1

Presiding: H. H. Goldsmith, Brookhaven National Laboratory, Upton, N. Y.

Proportional Counters—S. A. Korff, New York University, New York, N. Y.

Neutron Detection—H. L. Anderson, Institute for Nuclear Studies, University of Chicago, Chicago, Ill.

Ionization Chambers—J. A. Victoreen, Victoreen Instrument Company, Cleveland, O.

Ionization Chamber Measurements—E. W. Molloy, National Technical Laboratories, South Pasadena, Calif.

Stabilized High-Voltage Supply for Counters and Chambers—W. A. Higinbotham, Brookhaven National Laboratory, Upton, N. Y.

Electron Multiplier Counters—P. S. Johnson, Bureau of Ships, Navy Department, Washington, D. C.

Crystal Counters—R. Hofstadter, Palmer Physical Laboratory, Princeton University, Princeton, N. J.

Electronic Counting Techniques—M. Sands, Massachusetts Institute of Technology, Cambridge, Mass.

Photographic Emulsions for Use in Radiation Measurements—J. Spence, Research Laboratories, Eastman Kodak Company, Rochester, N. Y.

The conference will be held in the Engineering Societies Building, 33 W. 39 Street, New York. The AEC instrument exhibit, which will be located in the same building, will be open from 9 a.m. to 5:30 p.m. on November 30 and December 1. The exhibit will include 22 basic types of instruments for radiation detection in addition to a demonstration, using cut-away models, of various instrument techniques.

A copy of the complete program and advance registration blanks can be obtained from Prof. S. Fishman, Newark College of Engineering, 367 High Street, Newark 2, N. J. Registration at the conference will cost $4. The charge for advance registration will be $3.

AEC DESCRIBES ITS INTEREST IN THORIUM

Prompted by an increasing number of inquiries being received from individuals and small companies interested in monazite, the principal ore from which the element thorium is obtained, the Atomic Energy Commission has outlined for public information the nature and extent of its present interest.

While a strict control of exports and a complete record of domestic movements of thorium-bearing materials, including monazite ore, is maintained by the AEC, the usefulness of thorium and its principal source in nature, monazite ore, so far as the AEC's program is concerned, is limited for the present time to research. Accordingly, the only thorium the AEC purchases is for experimental purposes, chiefly in the form of thorium salts, and the AEC has no purchase program for monazite as such.

HAYES APPOINTED SAFETY DIRECTOR OF AEC

Daniel F. Hayes, former member of the staff of the American Standards Association, has been appointed Safety Director of the Atomic Energy Commission. During his five-year connection with the ASA, Mr. Hayes, who

holds a mechanical engineering degree from Rensselaer Polytechnic Institute and a law degree from Brooklyn Law School, was responsible for safety code work in the fields of personal equipment, exhaust ventilation, refrigeration, industial X-rays, and highway traffic.

WESTINGHOUSE OFFERS CHARTS ON ATOMIC SCIENCE

Six, two-color wall charts, presenting a "picture lesson" in atomic science, have been prepared by the Westinghouse Electric Corporation, Pittsburgh, Pa., for classroom use in schools and colleges. Measuring 25 by 36 inches, the charts are titled: Particles of Nuclear Physics, Structure of the Nucleus, Nuclear Reactions, Tools of the Nuclear Physicist, Using Nuclear Energy and Progress of Nuclear Physics.

The price of the complete set, including six charts and a 36-page supplementary booklet, is one dollar.

AEC, ONR TO SPONSOR 19 RESEARCH PROJECTS

Nineteen research projects in biology and medicine proposed by nongovernmental institutions in ten states have been selected for financial support by the Atomic Energy Commission. These projects will be administered by the Office of Naval Research under the joint program of support of fundamental scientific research previously announced by the AEC and ONR.

Listed below are the institution, subject of research and project director:

University of Colorado, Boulder: Study of relationships between chemical structure, physical characteristics and biological activity in the intermediate metabolism of nucleic acid derivatives (John R. Lacher), and Study of the radiation chemistry of bacteriophage invasion and reproduction in host cells (Theodore T. Puck); *Northwestern University, Evanston:* Establishment of a radioisotopic unit for instruction, research and therapy (J. Roscoe Miller); *Massachusetts Institute of Technology, Cambridge:* Radiomedicine research (Robley D. Evans); *Arnold Arboretum, Harvard University, Boston:* Dosage curves under varying conditions of time and intensity of radiation (Karl Sax); *College of Physicians and Surgeons, Columbia University, New York:* Effects of exposure to radioactive materials and to X-ray irradiation on nerve tissue (David Nachmonsohn).

N. Y. Post Graduate Hospital, New York: Skin changes produced by low-voltage roentgen-ray irradiations (Marion B. Sulzberger); *University of North Carolina, Chapel Hill:* Measurement of volume of flow of blood in the kidney and level of an unanesthetized man by means of radioisotopic procedure (H. D. Bruner); *Ohio State University, Columbus:* The establishment of physical and medical principles in the use of artificially radioactive cobalt-60 for the treatment of cancer (J. L. Morton); *Western Reserve University, Cleveland:* Medical and biological research on the toxicological effects of thorium and the comparative effects of various types of internally distributed ionizing particles (H. L. Friedell), and Intermediary metabolism on carbohydrates by bacteria (Harland G. Wood); *University of Oregon, Eugene:* Localization of radioactive isotopes in reproductive and germinal tissues during period of quiescence and activation (Arnold L. Soderwall and Paul Risley).

Oregon State College, Corvallis: The mode of action of 2-4-dichloro-phenoxyacetic acid as studied with the use of C^{14} (Joseph S. Butts), and A study of vitamin-amino acid and carbohydrate-amino acid relationships using C^{14} as a tracer substance (V. H. Cheldelin and B. E. Christensen); *University of Oregon Medical School, Portland:* The degradation of radioactive cholesterol fatty acids and ketone bodies in the animal

body (Edward S. West); *Baylor University, Waco:* Chemistry and metabolism of some sulfur oxides (Joseph H. Gast); *University of Texas, Austin:* Biological accumulation of inorganic materials by algae (Jack Myers); *University of Washington Medical School, Seattle:* The biological effects of radioactive sulfur (Robert H. Williams); *University of Wisconsin Medical School, Madison:* Labeled Azo Dye Research (James A. Miller).

Future Issues Will Feature . . .

NEUTRON DISTRIBUTIONS IN ELEMENTARY DIFFUSION THEORY

. . . by *P. R. Wallace*

A systematic presentation of solutions of standard neutron diffusion problems for engineers and physicists concerned with the wide range of reactor problems in which the elementary diffusion theory gives results of practical usefulness

NUCLEAR PHYSICS AND LOW TEMPERATURES

. . . by *M. E. Rose*

A survey of some recent developments connecting nuclear physics with research in low temperatures, and resulting in the adoption of new techniques in these two fields

NUCLEAR AND PHYSICAL PROPERTIES OF BERYLLIUM

. . . by *P. Barrett, J. R. Low, J. P. Howe*

A review of declassified theory and experimental data on the properties of beryllium and its alloys in relation to the use of this metal in nuclear reactors

NUCLEAR REACTOR ENGINEERING

. . . by *Lee Ohlinger*

First in a series of articles treating the design and construction of nuclear reactors, based on lectures for engineering students

NEUTRON DIFFRACTION IN THEORY AND EXPERIMENT

. . . by *A. H. Weber*

A detailed discussion of the neutron velocity selector, comparison of neutron diffraction with X-ray and electron diffraction, and phases of neutron diffraction work not yet fully described in the literature

THE PREPARATION AND USE OF NEUTRON SOURCES

. . . by *K. J. McCallum*

Theory and technique of neutron sources, with practical precautions to govern their use

BETA- AND GAMMA-RAY SPECTROSCOPY

. . . by *Gerald J. Hine*

A two-part review of different types of beta-ray spectrographs, the Fermi theory and Sargent diagram, electron and positron spectra, internal conversion lines, and determination of gamma-ray energies by photo- and Compton-electrons

ABSTRACTS

CHEMICAL PUBLICATIONS

Mass spectra of some organic compounds, R. H. Roberts, S. E. J. Johnsen (Monsanto Chemical Co., Texas City, Texas), *Anal. Chemi.* **20,** 690–699 (1948). The mass spectra of 53 organic compounds are given.

Depolymerization of butylene polymers, F. G. Cinpetta, S. J. Macuga, L. N. Leum (The Atlantic Refining Co., Philadelphia, Pa.), *Anal. Chemi.* **20,** 699–704 (1948). The catalytic depolymerization of butylene polymers over Attapulgus clay was studied by hydrogenation of feed and liquid products to paraffins, fractional distillation, and analysis of the fractions with a mass spectrometer.

Determination of position of tracer atom in a molecule: Mass spectra of some deuterated hydrocarbons, J. Turkevich, L. Friedman, E. Solomon, F. M. Wrightson (Princeton Univ., Princeton, N. J.), *J. Am. Chem. Soc.* **70,** 2638–2643 (1948). Monodeuteromethane, tetradeuteromethane, monodeuteroethane, monodeuteropropane-1, and monodeuteropropane-2 were synthesized and their mass spectra were determined. The mass spectrum of monodeuteromethane and of monodeuteroethane may be calculated from the mass spectra of methane and ethane, respectively, using the assumption of equal probability of rupture of hydrogen-carbon bonds, a $\frac{7}{6}$ factor for a carbon-hydrogen bond on a carbon atom that has deuterium and a $\frac{1}{2}$ factor for a carbon-deuterium bond. If D and H are removed simultaneously, these factors are not used. The position of the tracer atom in a propane molecule may be determined by an examination of the intensities of masses 30 and 16.

Observations on the production of mesons by cosmic radiation, G. P. S. Occhialini, C. F. Powell (Univ. of Bristol, England), *Nature* **162,** 168–173 (1948). Photographic plates exposed at high altitudes contained twenty nuclear explosions which were accompanied by the emission of slow mesons. The observed secondary effects produced by these mesons indicates that at least the majority of them interact with nuclei and are therefore negatively charged. These mesons have a high probability, when reduced to low velocities, of producing nuclear disintegrations of both light and heavy elements, with the emission of heavy particles.

Photodisintegration of the deuteron, R. Wilson, C. H. Collie, H. Halban (Clarendon Lab., Oxford, England), *Nature* **162,** 185–186 (1948). The total cross section for the photodisintegration of the deuteron into a proton and a neutron was measured by direct counting of the photoprotons in an ionization chamber filled with deuterium to a pressure of six atmospheres using a calibrated source of radiothorium. The cross section was found to be equal to $16.2 \pm 1.0 \times 10^{-28}$ cm^2, which favors a light meson mass.

Nuclear isomeric transitions of short periods, P. B. Treacy (Univ. of Sydney, Australia), *Nature* **162,** 186–187 (1948). Copper, molybdenum, silver, cadmium, indium and lead were irradiated by a pulsed beam of X-rays, and activity due to metastable states was sought in the intervals between pulses. The electrons producing the X-ray pulses had energies up to 1.05 Mev, the pulse width was 5 μsec, and the repetition frequency was 200 per sec. No evidence of activity was obtained, although periods greater than 100 μsec could have been detected.

Properties of a hypothetical di-neutron, N. Feather (Univ. of Edinburgh, Scotland), *Nature* **162,** 213 (1948). The half-time of a di-neutron is calculated to be > 1 and < 5 sec. It is suggested that the neutron bombardment of beryllium might be a convenient reaction in which to look for the di-neutron, and that it might be detected by the activities induced in simple elements (He^6 in helium, Na^{25} in sodium, Rh^{105} in rhodium, AcC^{211} in bismuth), for some of which large capture cross sections might exist.

Decay scheme of Hf^{181}, J. Beneš, A. Ghosh, A. Hedgran, N. Hole (Nobel Inst. for Physics, Stockholm, Sweden), *Nature* **162,** 261–262 (1948). Using higher resolving power and thinner counter windows, the β-spectrum of Hf^{181} was remeasured. Delayed coincidence measurements were also made to study the reported metastable state. The results support the decay scheme previously proposed by the authors.

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Internal pair conversion, M. H. Wang (Gonville and Caius College, Cambridge, England), *Nature* **162,** 264 (1948). The coefficients of the internal pair conversion of γ-rays for the element $Z = 84$, assuming magnetic dipole radiation, have been calculated using Dirac's exact wave equation of the electron. For $h\nu = 2.62$ Mev, $I = 1.5 \times 10^{-3}$, and for $h\nu = 8.00$ Mev, $I = 5.6 \times 10^{-3}$. A plot of I against $h\nu$ connecting these two points and passing through the point ($I = 0$, $h\nu = 2mc^2$) is nearly a straight line.

Beta spectrum of tritium, S. C. Curran, J. Angus, A. L. Cockcroft (Univ. of Glasgow, Scotland), *Nature* **162,** 302–303 (1948). A new technique for rapid and accurate detection and energy measurement of β-rays was applied to the β-spectrum of tritium. The method which is satisfactory for the energy range 0.5 to 150 kev uses a proportional counter, containing an argon-methane mixture at a pressure of one atmosphere or more, connected to a high-gain linear amplifier. The output pulses are applied to the deflecting plates of a cathode ray tube and recorded by a moving-film camera. The size of the pulses is a true relative measure of the energy of the ionizing radiation involved. Radiation of known energy is used to calibrate the apparatus. The upper limit of the $_1H^3$ spectrum was found to be 16.9 ± 0.3 kev. A maximum appears on a Fermi plot for $_1H^3$ at 2.5 kev. An application of neutrino theory to the upper end of the spectrum indicates that the neutrino mass is less than $m/300$. Since there is no evidence of γ-radiation following β-emission, the atomic mass equation is given by: $_1H^3 - {}_2He^3 = 0.000018$.

The Atomic Energy Research Establishment—Harwell, *Nature* **162,** 317–320 (1948). A review of the purpose, progress and future plans of the Atomic Energy Research Establishment at Harwell, England.

Behavior of a particle of very small mass in a magnetic field, J. Thibaud (Inst. of Atomic Physics, Univ. of Lyons, France), *Nature* **162,** 329 (1948). For an ultra-relativistic particle of very small mass, significant magnetic moment, and charge, special considerations come into play which determine its observability.

Proton bombardment of fluorine, S. Devons, H. G. Hereward (Cavendish Lab., Cambridge, Eng.), *Nature* **162,** 331–332 (1948). Proton bombardment of F^{19} was studied using the (γ,n) reaction in Cu^{63} as a threshold detector to measure the capture γ-rays for the reaction: $F^{19} + H^1 \rightarrow Ne^{20*} \rightarrow Ne^{20} + h\nu$ (12.8 Mev). The yield of γ-rays for the accompanying reaction $Ne^{20*} \rightarrow O^{16*} + He^4$; $O^{16*} \rightarrow O^{16} + h\nu$ (6 Mev) was measured simultaneously. A sharp rise in yield of 12.8 Mev γ-rays, as well as 6-Mev γ-rays, at proton energies between 630 and 700 kev was observed. The angular distribution of the capture γ-ray was found to be isotropic. The yield at the 660 kev resonance was estimated at $2.2 \pm 0.8\%$ of the 6-Mev γ-rays.

Polarization of annihilation radiation, R. C. Hanna (Cavendish Laboratory, Cambridge, England), *Nature* **162,** 332 (1948). The relative polarization of the two photons of 0.51 Mev energy produced in the annihilation of slow positions from Cu^{64} was studied. The results show that a relative polarisation does exist, but considerable quantitative discrepancies between theoretical predictions and experimental results were found.

Origin of cosmic ray stars, E. P. George (Birkbeck College, London), *Nature* **162,** 333 (1948). The range of the star-producing component of cosmic radiation expressed in g/cm² is larger by a factor of approximately 3 in lead than it is in air. Assuming this difference in range to be caused by the difference in the atomic weight of the two materials, the calculated value of the ratio of the range in lead to that in air is 2.5. The primaries may thus be stable particles having a cross section for star production given by the geometric cross section. These stable particles may be fast protons.

. . . I. W. RUDERMAN

LIFE SCIENCE PUBLICATIONS

The determination of residues of applied phospholipids and sodium *N*-alkyl sulfates on rat skin using radioactive tracer, R. Thomas, L. Edwards, J. Christian (School of Pharmacy, Purdue Univ., Lafayette,

Ind.) *J. Am. Pharm. Assoc.* **37,** 329–331 (1948). Techniques employed and results obtained are tabulated.

The utilization of labeled glycine in the process of amino acid incorporation by the protein of liver homogenate, T. Winnick, F. Friedberg, D. Greenberg (Div. of Biochemistry, Univ. of California Med. School, Berkeley) *J. Biol. Chem.* **175,** 117-126 (1948). The process of incorporation of labeled glycine into the protein of cell-free homogenates of rat liver appears to be enzymatic in nature. The rate of incorporation is dependent upon the glycine concentration, time of reaction and the *p*H of the medium. The enzyme system involved is associated with the insoluble particles of the homogenate. The process is promoted by certain inorganic ions.

Distribution of radioactive carbon among certain amino acids of liver homogenate protein following uptake experiments with labeled glycine, T. Winnick, I. Moring-Claesson, D. Greenberg (Div. of Biochemistry, Univ. of California Med. School, Berkeley) *J. Biol. Chem.* **175,** 127–132 (1948). Radioactive protein derived from the incubation of liver homogenate and labeled glycine was hydrolyzed and analyzed for its radioactive components. Isolation experiments using non-radioactive carriers showed that only 11 to 12% of the protein radioactivity was due to glycine. Approximately 60% of the activity was found in serine derived from glycine. Low concentrations were found in glutamic and aspartic acids and in arginine. None was found in alanine.

A method for the measurement of radioiodine in biological materials, M. Barry (Dept. of Pharmacology, Yale Univ. School of Med., New Haven) *J. Biol. Chem.* **175,** 179–185 (1948). A method is described for measuring radioiodine content in normal rat thyroid.

Incorporation *in vitro* of radioactive carbon from carbonyl-labeled D,L-alanine and glycine into proteins of normal and malignant rat livers, P. Zamecnik, I. Frantz, Jr., R. Loftfield, M. Stephenson (Medical Laboratories, Collis P. Huntington Memorial Hosp., Harvard Univ., at the Massachussetts General Hospital, Boston) *J. Biol. Chem.* **175,** 299–314 (1948). The rate of uptake of radioactivity in surviving slices of hepatoma nodules was 7 times that of normal liver slices and 2½ times that of slices of non-malignant portions of hepatoma-bearing livers. The bulk of the activity incorporated was accounted for by the alanine fraction of the proteins.

The determination of radioactive iron in biological material with particular reference to purification and separation of iron with isopropyl ether, ashing and electroplating technique, and accuracy of the method, G. Vosburgh, L. Flexner, D. Cowie (Dept. of Obstetrics, The Johns Hopkins Univ. and Hospital, Baltimore, Md.) *J. Biol. Chem.* **175,** 391–404 (1948). A method is presented for the determination of radioactive iron in biological material including carcass. Dry-ashing is employed. Isopropyl ether is used to purify radioiron and to separate iron from substances that interfere with electrodeposition. Recovery of known amounts of iron added to samples of various materials is complete.

Concerning the mechanism of the mammalian conversion of tryptophan into kynurenine, kynurenic acid and nicotinic acid, C. Heidelberger, M. Gullberg, A. Moran, S. Lepkovsky (Dept. of Chemistry and the Radiation Lab., Univ. of California, Berkeley) *J. Biol. Chem.* **175,** 471–472 (1948). D,L-Tryptophan, labeled with C^{14} in the beta position was administered to rats, dogs and rabbits. From the position of the label in the isolated kynurenine and kynurenic acid, the degradative reactions involved can be formulated. The *N*-methylnicotinamide isolated was devoid of activity, showing that nicotinic acid could not have been produced from tryptophan via oxidation of kynurenic acid.

Clinical and laboratory studies on the uptake of radioactive phosphorus by lesions of the breast, H. McCorkle, B. Low-Beer, H. Bell, R. Stone (Divisions of Radiology and Surgery, Univ. of California Med. School, Berkeley) *Surgery* **24,** 409–415 (1948). Geiger-Müller counter measurements of radioactivity made over breast lesions following administration of tracer doses of P^{32} give useful data for the clinical, radiologic and pathologic study of breast lesions. The method cannot be used at present for radiation therapy of breast lesions.

. . . BERNARD KANNER

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PHYSICAL PUBLICATIONS

Calculation of the ground state of the alpha particle, N. Svartholm, *Arkiv Mat. Astron. Fysik* (Stockholm) **35A,** No. 8, 1–16 (1948). An iteration method for the solution of nuclear eigenvalue problems is used to calculate the binding energy as a function of various parameters representing the different kinds of forces. If the range of nuclear forces is assumed on the basis of *p-p* scattering, the binding energies of the triton and alpha particle cannot be explained simultaneously.

Measurements of neutron intensities by means of a boron-lined ionization chamber, H. von Ubisch, *Arkiv Mat. Astron. Fysik* **35A,** No. 11, 1–9 (1948). An ionization chamber lined with boron and shielded with paraffin was used with a cyclotron. It served to increase the response to cyclotron radiation by a factor of 50 over an unlined chamber. Calibration in terms of a Ra-Be source was made, but the chamber counts mainly the gamma rays from such a source.

Radiations from Mg^{27} and Al^{28}, J. Beneš, A. Hedgran, N. Hole, *Arkiv Mat. Astron. Fysik* **35A,** No. 12, 1–8 (1948). The beta and gamma radiations were studied with a magnetic lens spectrometer. The Mg^{27} gave two beta groups with maximum energies 1.80 and 0.90 Mev, and gamma rays (using photoelectrons from a lead foil radiator) of 0.835 and 1.01 Mev. Al^{28} gave a 3.01-Mev beta ray and a 1.80-Mev gamma ray. Disintegration schemes are given.

Compteur à scintillations pour particules atomiques, T. Kahan, J. Debiene, R. Champeix, H. Bizot (Collège de France), *J. phys. radium* **9,** 25–26 (1948). A scintillation counter followed by an electron multiplier was used to detect alpha particles falling on a fluorescent crystal (zinc sulfide).

Sur le problème du proton et du neutron, V. S. Vrkljan, *J. phys. radium* **9,** 26–32 (1948). Modification of the Dirac theory and its extension to heavy particles, together with the use of wave packets, gives the values of the magnetic moments of the proton and neutron. Three charges are allowed for the proton and two for the neutron.

Les réactions thermonucleaires aux grandes densités (gaz dégénérés et non dégénérés), E. Schatzman (Institut d'Astrophysique de Paris), *J. phys. radium* 9, 46–60 (1948). Nuclear reactions in white dwarf stars at very high temperature were investigated, in particular the reaction $H^1 + H^1 \rightarrow H^2 + e^+$.

Depositif de synchronisation automatique du cyclotron, P. Debraine, C. Simane, *J. phys. radium* **9,** 113–121 (1948). A magnetic field regulator is described which superimposes a small oscillation on the static field and then automatically moves in such a direction as to achieve resonance.

Le spectre de densité des grandes gerbes atmospherique (gerbes d'Auger), A. Loverdos, J. Daudin (École Normale Superieure), *J. phys. radium* **9,** 134–136 (1948). The large air showers were investigated at 2,900 meters, using counters arranged so as to have areas up to 2,500 cm^2, in various coincidence arrangements. These gave the relation between the density and the extension of the showers.

L'hypothèse d'une particule intermédiare légère (méson λ) dans les grandes gerbes cosmiques de l'air (gerbes d'Auger). Étude à la chambre de Wilson, J. Daudin (Observatoire du Pic du Midi, Bagneres-de-Bigorre, France), *J. phys. radium* **9,** 137–142 (1948). The hypothesis of a light meson (about three times the electron mass) is used to explain the fact that the scattering of secondaries in Auger showers demands a higher mean energy than that given by the cascade theory of electrons and photons. Certain photographs of Auger showers indicate the existence of the light meson.

Calcul semi-quantique du spectra de rayonnement dans un accélerateur circulaire, à électrons, A. Abragam, *J. phys. radium* **9,** 143–146 (1948). The semi-quantum mechanical calculation of the spectrum of radiation from electrons accelerated in a circular path is found to give the same result as the classical calculation.

Sur la désintegration du meson, C. Marty (Collège de France), J. Prentki (Institut Henri-Poincare), *J. phys. radium* **9,** 147–149 (1948). The probability of disintegration of a π-meson of spin 1 into two μ-mesons of spin $\frac{1}{2}$ is calculated. Using Møller's meson theory to get the coupling

constants between the two types of meson, a lifetime of 10^{-8} to 10^{-9} sec was obtained. The beta disintegration of the μ-meson is also considered.

Nuclear spins of the carbon isotopes, F. A. Jenkins (Univ. of California, Berkeley), *Phys. Rev.* **74,** 355–363 (1948). The alternating intensities in the Swan bands of diatomic carbon were investigated with enriched samples. The spin of C^{13} was found to be $\frac{1}{2}$; that of C^{14} was found to be 0.

The slow neutron cross section of H, W. B. Jones (Cornell Univ., Ithaca, N. Y.), *Phys. Rev.* **74,** 364–369 (1948). The total cross sections of water and cyclohexane in the energy intervals 0.003 to 100 ev and 0.08 to 100 ev, respectively, were determined with the Cornell slow neutron velocity spectrometer. Oxygen and carbon cross sections were also measured so that subtraction would give the neutron-proton cross section. Taking account of the anisotropic binding of hydrogen to oxygen or carbon, the free neutron-proton cross section was found to be $20.1 \pm 0.03 \times 10^{-24}$ cm^2. The mean vibration energy of bound hydrogen was measured as 0.3 ev.

Reaction constants for $Li^7(p,n)Be^7$, R. Taschek, A. Hemmendinger (Los Alamos Scientific Lab., Los Alamos, N. M.), *Phys. Rev.* **74,** 373–385 (1948). The absolute value of the reaction cross section for various proton energies (1.95 to 2.25 Mev) was determined by bombardment of thin lithium targets, using an electrostatic generator, and by comparison of the resulting neutron flux with a standard RaBe source, using the activity produced by the neutrons in a "manganese bath." The angular distribution of the neutrons from the reaction was measured with a counter whose response was nearly energy-independent and with a second counter at zero degrees to the beam as a monitor. The same energy region was covered for these measurements.

Resonances in $Li^7(p,n)Be^7$, G. Breit, I. Bloch (Yale Univ., New Haven, Conn.), *Phys. Rev.* **74,** 397–404 (1948). The theory of the angular distribution of the neutrons from this reaction is presented and, from the experimental evidence, the existence of a quasi-stationary state at 2.2 Mev proton energy and another (less certain) below threshold. These levels probably are of odd parity.

Angular distribution of alphas from $Li^6(d,\alpha)\alpha$ and $Li^7(p,\alpha)\alpha$, N. P. Heydenburg, C. M. Hudson, D. R. Inglis, W. D. Whitehead (Carnegie Institution of Washington, Washington, D. C.), *Phys. Rev.* **74,** 405–410 (1948). Because of the Bose statistics of the alpha particles produced, the angular distribution may be expanded in even powers of the cosine of the scattering angle. An electrostatic generator gave the bombarding protons, and a proportional counter detected the alphas. Excitation curves, obtained by measuring the yield at 90° to the bombarding beam, are given as a function of proton energy. The variation of the angular distribution is given by plotting the coefficients of the terms in $\cos^2$ and $\cos^4$ as a function of energy. These coefficients for the $Li^7(p,\alpha)\alpha$ reaction are compared with theoretical formulas.

Discharge spread in Geiger counters with methane and methane/argon fillings, C. Balakrishnan, J. D. Craggs, A. A. Jaffe (Metropolitan-Vickers Electrical Company, Manchester, England), *Phys. Rev.* **74,** 410–414 (1948). A counter tube containing six counters separated by thin glass windows was used. The counter at one end was irradiated with gamma rays, and coincidences with the others along the line were measured thus giving the percent discharge spread as a function of the distance along the counter. The results indicate that photo-ionizing radiations are produced mainly in the argon and quenched by the methane when both are present.

Penetrating particles in extensive air showers, J. E. Treat, K. I. Greisen (Cornell Univ., Ithaca, N. Y.), *Phys. Rev.* **74,** 414–423 (1948). Penetrating particles in extensive air showers were investigated at two altitudes. The number penetrating various thicknesses of lead are given. A strong reduction in the density of the penetrating particles between the two elevations excludes the hypothesis that they are mesons produced near the top of the atmosphere in the act initiating the shower. The penetrating particles, and the primaries which produce them if they are locally produced, do not have a very great range in lead. No evidence was found for production of groups of penetrating particles in a lead shield by the particles in extensive air showers.

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The beta- and gamma-spectra of gallium irradiated by slow neutrons, S. K. Haynes (Oak Ridge National Lab., Oak Ridge, Tenn.), *Phys. Rev.* **74,** 423–432 (1948). The spectrum of Ga^{72} as investigated on a thin-lens spectrometer showed beta-ray groups with endpoints at 3.15, 2.52, 1.48, 0.955, and 0.64 Mev. Gamma rays were found at 2.51, 2.21, 1.87, 1.59, 1.05, 0.84, and 0.63 Mev, with a conversion line at 0.68 Mev. A tentative disintegration scheme is given, showing seven levels in the residual nucleus. The spectrum of Ga^{76} (20.5 min) is a simple beta ray, showing a linear Kurie plot from the endpoint (1.65 Mev) down to 0.4 Mev.

Phenomenological theory of exchange currents in nuclei, R. G. Sachs (Univ. of Wisconsin, Madison), *Phys. Rev.* **74,** 433–441 (1948). A flow of charge (exchange current) between nucleons is theoretically shown to follow from the charge exchange nature of their interaction potentials. A calculation was made of the resulting magnetic moment and of the transition probabilities for absorption and emission of radiation.

Relative yields of some X-ray induced nuclear reactions, M. L. Perlman, G. Friedlander (General Electric Company, Schenectady, N. Y.), *Phys. Rev.* **74,** 442–448 (1948). Various targets were bombarded with 100-Mev and 50-Mev X-rays from betatron and synchrotron, in order to determine relative yields of (γ,n), (γ,p), $(\gamma,2n)$, and $(\gamma,2p)$ reactions. The yields were measured with G-M counters to record the activities. Irradiations were monitored by measurement of C^{11} or F^{18} activity produced in a standard piece of polystyrene or lithium fluoride. Self-absorption corrections were experimentally determined. A sudden increase occurred in the (γ,n) yield at about mass 60. The (γ,p) yields were all about the same as the (γ,n) yield for the light elements. The two-particle yields were all much lower than the single-particle yields.

Photographic plates for use in nuclear physics, J. H. Webb (Eastman Kodak Company, Rochester, N. Y.), *Phys. Rev.* **74,** 511–532 (1948). The stopping-powers and range-energy relations for alpha particles, deuterons, protons, mesons, and electrons in photographic plates were derived on the basis of the general theory of energy-loss by charged particles. Grain density is discussed for various particles, and calibration of various types of plate analyzed. In silver bromide, consideration of the energy required to produce an ion pair shows that about 150 ion pairs must be produced in a single grain to produce a latent image.

Study of the beta spectra of C^{14} and S^{35}, C. S. Cook, L. M. Langer, H. C. Price (Indiana Univ., Bloomington), *Phys. Rev.* **74,** 548–552 (1948). The beta spectra of C^{14} and S^{35} were measured in a large double-focusing spectrometer, using sources of high specific activity. The source thicknesses were 40–170 micrograms/cm² for S^{35}, and 130–970 micrograms/cm² for C^{14}, with backings of 20 micrograms/cm² of Zapon. The S^{35} spectrum deviates from that predicted by the Fermi theory for an allowed spectrum for energy below 1.15 mc^2. The shape of this spectrum at the upper end sets an upper limit of 1 % of the electron mass to the mass of the neutrino. The spectrum of C^{14} gives an approximately linear Kurie plot down to 1.15 mc^2, showing a very slight concavity toward the energy axis. This is not consistent with the shape calculated for a second forbidden transition using Fermi selection rules.

The scattering of 2.4 to 3.5-Mev protons by protons, J. M. Blair, G. Freier, E. E. Lampi, W. Sleator, J. H. Williams (Univ. of Minnesota, Minneapolis), *Phys. Rev.* **74,** 553–561 (1948). An electrostatic generator provided protons of known energy which were directed onto a scattering chamber containing hydrogen. The proton beam was monitored by a current collector, and the scattered protons were detected by a proportional counter. Results on the cross section per unit solid angle for protons of energy 2.42, 3.04, 3.27, and 3.53 Mev are given. The experiments confirm and extend the earlier data on proton-proton scattering in the energy region where *S*-wave nuclear interaction is preponderant.

The specific primary ionization and energy loss of fast electrons in matter, F. L. Hereford (Bartol Research Foundation, Franklin Institute, Swarthmore, Pa.), *Phys. Rev.* **74,** 574–579 (1948). Using a beta-ray spectrometer from 0.2 to 0.75 Mev, and a coincidence method up to 9.0 Mev, the specific primary ionisation of hydrogen was determined by means of the dependence of Geiger counter efficiency on that quantity. The results agree quite well with Bethe's theory. The value of the

specific primary ionization in condensed substances was also measured by interposition of samples of water and carbon. The ratio of the specific primary ionization of these substances definitely favors the Halpern-Hall over the Bethe-Bloch theory. The specification of the path length through the counter at low energy was accomplished by normalization with the high-energy data.

Shower production by penetrating particles at 14,000 feet, H. Bridge, W. Hazen (Massachusetts Inst. of Technology, Cambridge, Mass.), *Phys. Rev.* **74,** 579–591 (1948). Showers produced by penetrating particles at 14,000 feet were studied with various arrays of G-M counters, cloud chamber, and ionization chamber. Most of the observed showers generated in a five-inch lead absorber contained heavier particles as well as energetic electrons, indicating their production from a nuclear disruption. The initiating particles were not electrons, and their relative frequency at high and low altitudes showed that they were not ordinary mesons.

Measurements of the east-west asymmetry of cosmic rays at Hobart, Tasmania, A. G. Fenton, D. W. P. Burbury (Univ. of Tasmania, Hobart, Tasmania, Australia), *Phys. Rev.* **74,** 589–591 (1948). A Geiger counter telescope directed at a zenith angle of 45° shows an east-west asymmetry at a geomagnetic latitude of 51.7° south, amounting to 0.008 without, and 0.019 with 12.5 cm of lead. The increase with the lead shield indicates that the asymmetry in these latitudes is due to the hard component of the radiation.

A new radioactive series—the protactinium series, M. H. Studier, E. K. Hyde (Argonne National Lab., Chicago, Ill.), *Phys. Rev.* **74,** 591–600 (1948). The existence of a branch of the uranium-radium series consisting of a whole series of synthetically produced isotopes. Deuteron and alpha-particle bombardment of thorium gives the parent, Pa^{230}. The isotopes, their lifetimes, and the energy and nature of their radiations are given.

Radiations from platinum (193) and gold (199), C. E. Mandeville, M. V. Scherb, W. B. Keighton (Bartol Research Foundation, Franklin Institute, Swarthmore, Pa.), *Phys. Rev.* **74,** 601–605 (1948). Neutron irradiation of platinum in the Oak Ridge pile produced the isotopes, which were investigated by absorption in aluminum and lead, and beta-beta, beta-gamma, and gamma-gamma coincidences. The platinum isotope showed conversion electrons of energy 0.115 Mev, apparently uncoupled to any gamma ray, and 70-kev X-rays. $^{*}Au^{199}$ has beta rays of maximum energy 0.38 Mev, with 0.18-Mev gammas indicated by lead absorption. A disintegration scheme is constructed, using the fact that there are beta-beta and beta-gamma, but no gamma-gamma coincidences present.

The excitation of nuclei by electrons, I. N. Sneddon, B. F. Touschek (Univ. of Glasgow, Scotland), *Proc. Roy. Soc.* **193,** 344–356 (1948). The cross section of electrons inelastically scattered by nuclei is assumed to come from electromagnetic interaction with protons (that associated with beta disintegration is shown to be small). Electric dipole and quadrupole and magnetic dipole transition correspond to cross sections which are calculated. Comparison with experiment gives fair results except in the region where the Born approximation falls.

On the scattering of protons by protons, W. H. Ramsey (Univ. of Manchester, England), *Proc. Roy. Soc.* **194,** 228–237 (1948). The Moller-Rosenfeld mixed meson theory is used to calculate the proton-proton scattering. The phase shifts are calculated by various methods for different energies and meson masses. The comparison of the results with experiments on scattering of slow and fast protons indicates a meson mass of 270–300 electron masses and a nuclear interaction between protons of 2% less than that between neutron and proton. The ^3P phase shift at 10 Mev requires a meson mass of 350 electron masses to account for the experimental value. The discrepancies lead to the suggestion of modifications of the M-R theory.

Some Geiger-Müller and proportional counters of spherical shape, G. Salvini (Instituto di Fisica Superiore, Univ. of Milan, Italy), *Rev. Sci. Instr.* **19,** 494–496 (1948). Counters are described with spherical cathodes and wire-ring anodes. Geiger counters with argon-alcohol fillings show 100-volt plateau with slope of 10% per hundred volts. They are suitable for coincidence work on cosmic rays, with their symmetry giving a special advantage. Filling them with a BF_3 mixture allows the construction of a proportional counter for slow neutrons.

On cloud-chamber valves, F.-H. Chu, G. E. Valley (Massachusetts Inst. of Technology, Cambridge, Mass.), *Rev. Sci. Instr.* **19,** 496–499 (1948). The effect of opening a valve by using an auxiliary coil to release an iron armature from a permanent magnet was investigated. By discharging a condenser through a cold-cathode tube and the triggering coil, the time required to open the valve is materially reduced (two to ten times, depending on valve size). It is made also less dependent on the pressure and current. Dependence on the electrical and magnetic circuits is discussed. It is found possible to make valves whose opening time is limited by mechanical rather than electrical and magnetic parameters.

A new quenching circuit for Geiger counters, H. Maier-Leibnitz (Kaiser Wilhelm Institut für Medizinische Forschung, Institut für Physik, Heidelberg, Germany), *Rev. Sci. Instr.* **19,** 500–502 (1948). A quenching circuit is described which works on the multivibrator principle but uses separate grids for signal and feedback. The oscillation takes 0.2 millisecond, and the voltages are restored within one-tenth of this time after the oscillation. Thus the quenching circuit is always operative during the counting time and the correction for dead time is simplified.

Electromagnetic deflector for the beam of the 184-inch cyclotron, W. M. Powell, L. R. Henrich, Q. A. Kerns, D. C. Sewell, R. L. Thornton (Univ. of California, Berkeley), *Rev. Sci. Instr.* **19,** 506–512 (1948). For a large frequency-modulated cyclotron the usual deflector is impractical because of the small increase in radius per turn. A pulsed electric deflector was designed which gave as much as 7 cm additional radial oscillation to the beam, enabling ions to reach a magnetic deflector. About ½ % of the circulating beam reaches the external beam.

Circuit for testing efficiency of Geiger counters, G. E. Hagen, D. H. Loughridge (Univ. of Washington, Seattle), *Rev. Sci. Instr.* **19,** 526–528 (1948). An electronic apparatus is described which will test the efficiency of Geiger tubes of a wide variety, or the relative efficiency of different parts of a single tube. The method involves double and triple coincidence rates among three tubes of similar type, and comsic rays may be used as a source.

. . . HAROLD BROWN

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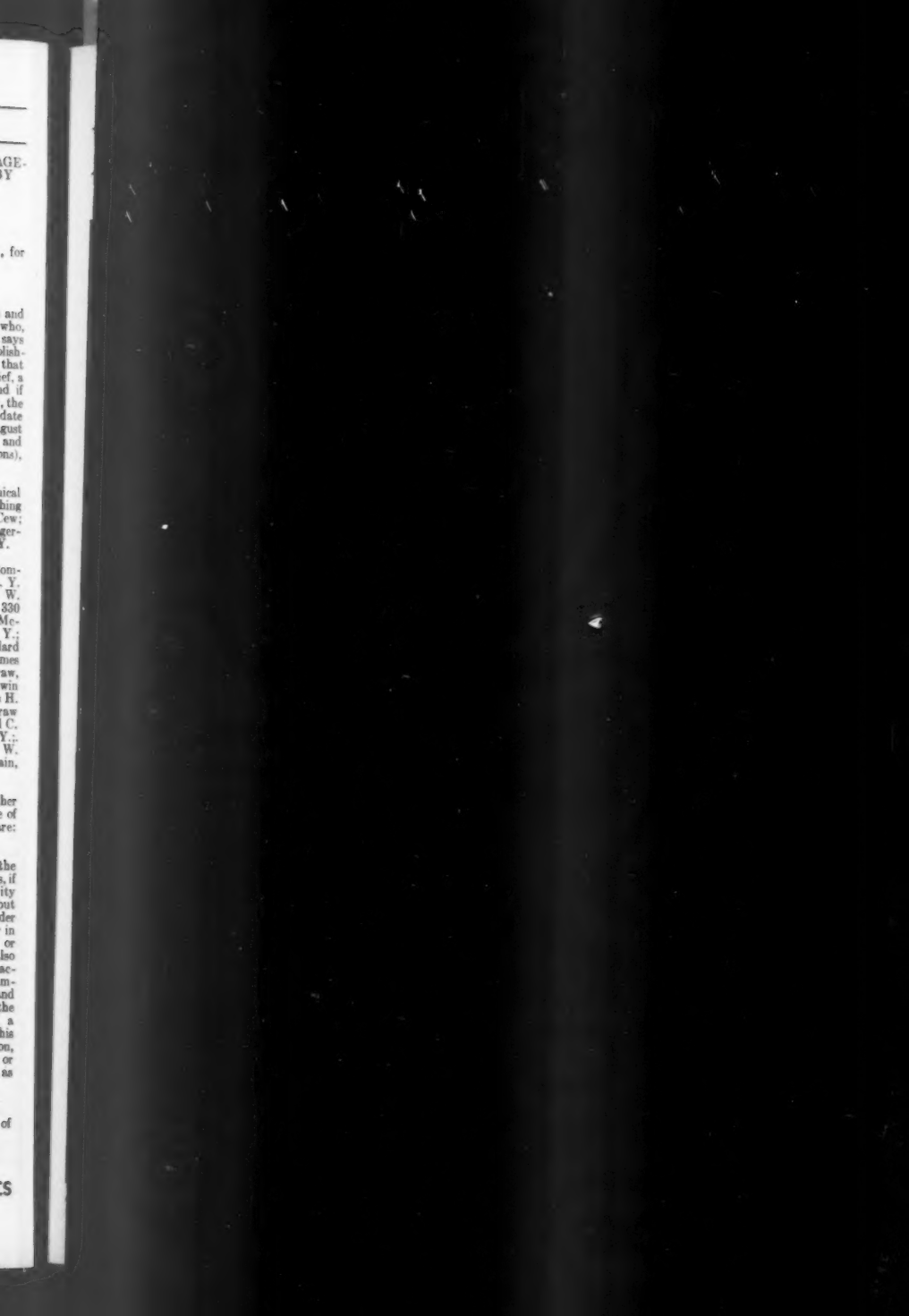
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